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(54) [Title of the Invention]

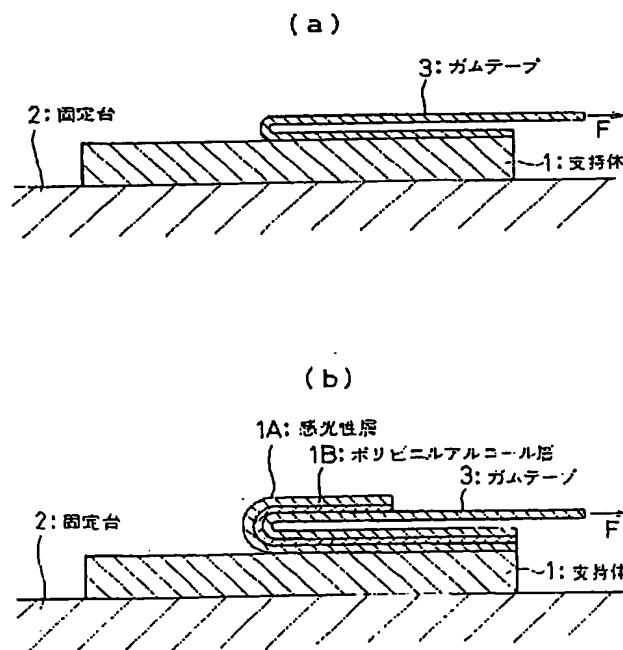
PRINT-DEVELOPABLE LIGHT-SENSITIVE LITHOGRAPHIC PRINTING PLATE  
PRECURSOR AND PROCESS FOR MAKING PRINTING PLATE THEREFROM

(57) [Abstract]

[Problem] To provide a print-developable light-sensitive lithographic printing plate excellent in press life, sensitivity and image reproducibility.

[Means for Solution] A print-developable light-sensitive lithographic printing plate precursor comprising an ink-receptive photosensitive layer containing a compound having at least one addition-polymerizable ethylenically double bond and a photopolymerization initiation system provided on a hydrophilicized support, wherein the support

exhibits a gummed tape peel strength of 500 g/cm or less. The print-developable light-sensitive lithographic printing plate precursor is imagewise exposed to light. The printing plate is then mounted on the cylinder of a printing machine. The printing plate is then supplied with a printing ink. The unexposed area of the photosensitive layer is then transferred with the ink to the surface of a blanket roller using the adhesivity of the ink to remove the unexposed area from the support and form a photosensitive image.



[Claims]

1. A print-developable light-sensitive lithographic printing plate precursor comprising an ink-receptive photosensitive layer containing a compound having at least one addition-polymerizable ethylenically double bond and a photopolymerization initiation system provided on a hydrophilicized support, wherein the peel strength of a gummed tape with respect to the support as determined by a peel strength measurement method using a gummed tape is 500 g/cm or less.

2. The print-developable light-sensitive lithographic printing plate precursor as defined in Claim 1, wherein the peel strength of a gummed tape with respect to the support of the unexposed photosensitive layer as determined by a peel strength measurement method using a gummed tape is from 0.5 to 200 g/cm.

3. The print-developable light-sensitive lithographic printing plate precursor as defined in Claim 1 or 2, wherein the peel strength of a gummed tape with respect to the support of the exposed photosensitive layer as determined by a peel strength measurement method using a gummed tape is greater than 200 g/cm.

4. A plate making process which comprises imagewise exposing the photosensitive layer of a print-developable light-sensitive lithographic printing plate precursor as defined in any one of Claims 1 to 3 to light in the wavelength

range of from ultraviolet to near infrared so that the photosensitive layer is imagewise photo-set, and then removing the unexposed area of the photosensitive layer from the support to form a photo-set photosensitive image, characterized in that when a printing ink is supplied onto the photosensitive layer of the imagewise exposed print-developable light-sensitive lithographic printing plate mounted on the cylinder of the printing machine from which it is then transferred to the surface of a blanket roller, the unexposed area is transferred with the ink to the surface of the blanket roller using the adhesivity of the ink to remove the unexposed area from the support.

5. A plate making process which comprises imagewise exposing the photosensitive layer of a print-developable light-sensitive lithographic printing plate precursor as defined in any one of Claims 1 to 3 to light in the wavelength range of from ultraviolet to near infrared so that the photosensitive layer is imagewise photo-set, and then removing the unexposed area of the photosensitive layer from the support to form a photo-set photosensitive image, characterized in that when a cover sheet is provided on the photosensitive layer of the print-developable light-sensitive lithographic printing plate precursor before or after the imagewise exposure and then peeled off from the photosensitive layer after the imagewise exposure, the unexposed area is transferred to the cover sheet using the adhesivity of the cover sheet to remove the unexposed

area from the support.

6. A process for making a printing plate from a print-developable light-sensitive lithographic printing plate precursor as defined in Claim 5, wherein when the cover sheet is peeled off from the photosensitive layer after the imagewise exposure to remove a part of the unexposed area from the support and on the cylinder of the printing machine is mounted the print-developable light-sensitive lithographic printing plate precursor the photosensitive layer of which is supplied with a printing ink which is then transferred to the surface of the blanket roller, the remaining unexposed area is transferred to the surface of the blanket roller with the ink using the adhesivity of the ink.

7. The process for making a printing plate from a print-developable light-sensitive lithographic printing plate precursor as defined in Claim 6, wherein the cover sheet is peeled off from the photosensitive layer after the imagewise exposure to remove the unexposed area such that from 0.1 to 50% by weight of the unexposed area remains in the support.

[Detailed Description of the Invention]

[0001]

[Technical Field to which the Invention Belongs]

The present invention relates to a print-developable light-sensitive lithographic printing plate precursor and a process for the preparation thereof. More particularly, the

present invention relates to a novel print-developable light-sensitive lithographic printing plate precursor capable of forming a photo-set photosensitive image without requiring alkaline development and a process for making a printing plate therefrom.

[0002]

[Related Art]

A related art photosensitive lithographic printing plate precursor comprises a negative-working photosensitive layer made of diazo resin, photolinkable polymer, photopolymerizable composition, etc. or a positive-working photosensitive layer made of benzoquinone diazide, naphthoquinone diazide, etc. spread over a hydrophilicized support and optionally a polyvinyl alcohol layer formed on the photosensitive layer as an oxygen barrier layer.

[0003]

In order to form a photosensitive image on such a photosensitive lithographic printing plate precursor (plate making), the printing plate is imagewise exposed to light, and then given a physical stimulation using a brush or the like while being dipped in an alkaline developer containing an organic alkaline agent such as sodium silicate and sodium carbonate or an organic alkaline agent such as diethanolamine and triethanolamine so that the photosensitive layer is dissolved away on the unexposed area in the case of negative-working

photosensitive layer or on the exposed area in the case of positive-working photosensitive layer.

[0004]

When the surface of the printing plate precursor having an image thus formed thereon is supplied with an ink solution comprising an emulsion of an ink-réceptive printing ink with a printing fountain solution, the difference in hydrophilicity between the surface of the exposed hydrophilic support and the photosensitive image causes the printing ink and water to be selectively attached to the photosensitive image and to the surface of the exposed hydrophilic support, respectively, to form a printing ink image. By transferring this printing ink image to an image-receiving paper, a printed matter can be obtained.

[0005]

The alkaline developer to be used in the aforementioned plate-making step is normally required in an amount of from 10 to 20 l (litter) for an automatic developing apparatus to obtain a uniform image. In general, the same developer is repeatedly used for the development of a large number of sheets of photosensitive lithographic printing plate precursors to suppress the rise of the used amount of the alkaline developer. The alkaline developer which has been thus repeatedly used is deteriorated with time by the photosensitive layer composition dissolved in the developer and oxygen in the air, making it



likely that underdevelopment can occur. In order to inhibit the deterioration of the alkaline developer, a complicated working for replenishing with a high concentration alkaline developer is required. Even when the replenishment with a high concentration alkaline developer is effected, it is required that the developer be renewed once per few weeks in an ordinary plate-making factory.

[0006]

When the alkaline developer is renewed, the used alkaline developer is discharged as a waste liquid. In recent years, from the standpoint of protection of marine environment, it has been difficult to discard the use alkaline developer into the sea. Thus, the disposal of the used alkaline developer has long been an important problem in the art of printing.

[0007]

To this end, a photosensitive lithographic printing plate precursor requiring no development with an alkaline developer has been under research and development. However, these related art products are disadvantageous in that none of them allow a sufficient distinction between ink-receptive image area and hydrophilic non-image area. As a result, these related art photosensitive lithographic printing plate precursors give a printed matter having a deteriorated image quality. These related art photosensitive lithographic printing plate precursors have an insufficient durability on the ink-receptive

image area and thus cannot be used for printing over an extended period of time. Further, the hydrophilic image-forming layer of these related art photosensitive lithographic printing plate precursors are susceptible to scratching and abrasion.

[0008]

As means of solving these problems, JP-A-8-48020 discloses a technique for preparing a lithographic printing plate from a photosensitive lithographic printing plate precursor comprising an ink-receptive radiation-absorbing heat-sensitive image-forming layer provided on a support having a porous hydrophilic surface in the following manner.

[0009]

(1) The photosensitive lithographic printing plate precursor is imagewise exposed to light so that heat is generated on the exposed area to enhance the adhesivity between the image-forming layer and the support. Thereafter, the image-forming layer is peeled off from the unexposed area to expose the porous hydrophilic surface.

[0010]

(2) The image-forming layer is irradiated with and absorbs infrared rays while a transfer sheet having an image-forming layer is in close contact with the support of the printing plate support so that the infrared rays are converted to heat by which the image-forming layer is transferred from the transfer sheet to the support of the printing plate precursor. Alternatively,

the image-forming layer provided on the support of the photosensitive lithographic printing plate precursor is similarly irradiated with light so that light is converted to heat by which the adhesivity between the image-forming layer and the support of the printing plate precursor is enhanced. The image-forming layer is peeled off from the unexposed area.

[0011]

[Problems that the Invention is to Solve]

The process for the preparation of a photosensitive lithographic printing plate involving the enhancement of the adhesivity of the image-forming layer provided on the support of a printing plate precursor with the support by the action of heat by exposure to light and the removal of the unexposed area is disadvantageous in that when a material having a high heat conductivity such as aluminum is used as a support of printing plate precursor, the heat generated by exposure to light diffuses efficiently, making little difference in thermal adhesivity to the support between the unexposed area and the exposed area on the image-forming layer and hence giving insufficient sensitivity.

[0012]

Further, the related art photosensitive lithographic printing plate precursors are exposed on the hydrophilic support and thus are subject to stain on the exposed hydrophilic area when the conveyance roller or fingers are brought into contact

with the hydrophilic area during the conveyance of the lithographic printing plate precursors or the mounting of the lithographic printing plate precursors on the printing machine, causing staining on the image area of printed matter during printing. Therefore, in the related art, a step of spreading an aqueous solution of hydrophilic polymer on the printing plate and then drying the printing plate to provide a protective layer is required to inhibit the attachment of such a stain and keep the non-image area hydrophilic.

[0013]

An aim of the invention is to solve the problems with the related art and hence provide a photosensitive lithographic printing plate precursor which requires no alkaline developer and exhibits a good sensitivity to a range of ultraviolet to near infrared.

[0014]

Another aim of the invention is to provide a photosensitive lithographic printing plate precursor excellent in printing properties such as affinity to printing ink and press life.

[0015]

A further aim of the invention is to provide a lithographic printing plate precursor which can be protected on the non-image area thereof until printing.

[0016]

[Means for Solving the Problems]

The print-developable light-sensitive lithographic printing plate precursor of the invention comprises an ink-receptive photosensitive layer containing a compound having at least one addition-polymerizable ethylenically double bond and a photopolymerization initiation system provided on a hydrophilicized support, wherein the peel strength of a gummed tape with respect to the support as determined by a peel strength measurement method using a gummed tape is 500 g/cm or less.

[0017]

In accordance with the aforementioned print-developable light-sensitive lithographic printing plate precursor, the peel strength of a gummed tape from the support of the unexposed photosensitive layer and the exposed photosensitive layer as determined by a peel strength measuring method using a gummed tape are preferably from 0.5 to 200 g/cm and 200 g/cm, respectively.

[0018]

In accordance with the aforementioned print-developable light-sensitive lithographic printing plate precursor, the unexposed area of the photosensitive layer can be transferred to the surface of a blanket roller or a cover sheet and thus can be easily removed by the use of the adhesivity of the printing ink or the cover sheet without using any alkaline developer according to the process of the invention. Further, the

hydrophilic surface of the support is protected by the unexposed area of the photosensitive layer until printing, making it easy to form a sharp image.

[0019]

The process for making a printing plate from a print-developable light-sensitive lithographic printing plate precursor of the invention comprises imagewise exposing the photosensitive layer of a print-developable light-sensitive lithographic printing plate precursor as defined in any one of Claims 1 to 3 to light in the wavelength range of from ultraviolet to near infrared so that the photosensitive layer is imagewise photo-set, and then removing the unexposed area of the photosensitive layer from the support to form a photo-set photosensitive image, characterized in that when a printing ink is supplied onto the photosensitive layer of the imagewise exposed print-developable light-sensitive lithographic printing plate mounted on the cylinder of the printing machine from which it is then transferred to the surface of a blanket roller, the unexposed area is transferred with the ink to the surface of the blanket roller using the adhesivity of the ink to remove the unexposed area from the support.

[0020]

Further, the plate-making process of the invention may be arranged such that when a cover sheet is provided on the photosensitive layer of the print-developable light-sensitive

lithographic printing plate precursor before or after the imagewise exposure and then peeled off from the photosensitive layer after the imagewise exposure, the unexposed area is transferred to the cover sheet using the adhesivity of the cover sheet to remove the unexposed area from the support.

[0021]

In this case, the plate-making process of the invention is preferably arranged such that when the cover sheet is peeled off from the photosensitive layer after the imagewise exposure to remove a part, preferably from 0.1 to 50% by weight, of the unexposed area from the support and on the cylinder of the printing machine is mounted the print-developable light-sensitive lithographic printing plate precursor the photosensitive layer of which is supplied with a printing ink which is then transferred to the surface of the blanket roller, the remaining unexposed area is transferred to the surface of the blanket roller with the ink using the adhesivity of the ink.

[0022]

In the invention, the peel strength with a gummed tape (hereinafter referred to as "gummed tape peel strength") indicating the surface adhesivity of the hydrophilicized support (hereinafter referred to as "hydrophilic support") is presented by the linear tension (g/cm) obtained by contact-bonding a gummed tape (SLION TAPE, produced by SLIONTEC)

onto the surface of a support 1 at 25°C, a pressure of 5 kg/cm<sup>2</sup> and a rate of 50 cm/min, fixing the support 1 onto a fixing table 2, determining the force F required to peel the gummed tape 3 off the support 1 at an angle of 180° at a rate of 30 cm/min, and then dividing the force F by the width of the gummed tape as shown in Fig. 1(a). The gummed tape peel strength indicating the adhesivity of the photosensitive layer with respect to the hydrophilic support is represented by the linear tension (g/cm) obtained by sequentially laminating a photosensitive layer 1A and a polyvinyl alcohol 1B having a thickness of 3 μm on the surface of the support 1, contact-bonding a gummed tape (SLION TAPE, produced by SLIONTEC) onto the surface of the support 1 at 25°C, a pressure of 5 kg/cm<sup>2</sup> and a rate of 50 cm/min, fixing the support 1 onto the fixing table 2, determining the force F required to peel the polyvinyl alcohol layer 1B and the photosensitive layer 1A bonded to the gummed tape 3 off the support 1 at an angle of 180° at a rate of 30 cm/min, and then dividing the force F by the width of the gummed tape as shown in Fig. 1(b).

[0023]

[Mode for Carrying Out the Invention]

Embodiments of implementation of the invention will be described in detail hereinafter.

[0024]

The hydrophilic support to be used in the invention is



covered with a thin water layer on the surface thereof (wet state) when supplied with a fountain solution during printing. Thus, the hydrophilic support is capable of inhibiting the attachment of lipophilic ink particles to form a non-image area on the printed matter during the contact with the printing ink in the form of emulsion as well as easily removing and transferring the photosensitive layer spread over the hydrophilicized surface onto the cylinder of the blanket roller by the adhesivity to the printing ink during printing.

[0025]

The hydrophilic support having these capacities is required to have a gummed tape peel strength of 500 g/cm or less required to peel a gummed tape off from the support according to the aforementioned gummed tape peel strength measuring method.

[0026]

Further, the gummed tape peel strength required to peel the unexposed photosensitive layer off from the hydrophilic support is preferably from 0.5 to 200 g/cm, more preferably from 1 to 150 g/cm, particularly from 2 to 100 g/cm, even more preferably from 10 to 100 g/cm. The gummed tape peel strength required to peel the exposed photosensitive layer off from the hydrophilic support is preferably 150 kg/cm or more, particularly greater than 200 kg/cm.

[0027]

More particularly, the hydrophilic support according to the invention may be either the following material (1) or (2).

[0028]

(1) Aluminum sheet obtained by subjecting the surface of an aluminum sheet to roughening (graining) in various manners and hydrophilicization by anodization or the like

(2) Support having an excellent dimensional stability made of various paper sheets such as paper, synthetic paper, coated paper and art paper, sheet of metal such as aluminum, copper, iron and stainless steel, wooden sheet, sheet of plastic such as polyethylene terephthalate, polypropylene or polyethylene or the like having a hydrophilic or swelling hydrophilic polymer layer provided thereon

The graining of the aluminum sheet (1) is conducted to enhance the adhesivity of the photosensitive layer formed on the support and hence improve the water wettability of the non-image area of the printing plate precursor. Graining has an effect on both the properties and durability of the printing plate. The quality of graining is an important factor determining the general quality of the printing plate. The formation of a pit-free fine uniform grain makes it possible to provide the resulting printing plate with essentially good printing properties.

[0029]

As such graining methods there are well known mechanical

and electric graining methods. These methods are widely used in the production of lithographic printing plates. The use of an electrolytic graining method called electrochemical graining or electrochemical roughening makes it possible to obtain good results.

[0030]

For the production of lithographic printing plates, many electrolytic graining methods have been already proposed as disclosed in US Patents 3,755,116, 3,887,447, 3,935,080, 4,087,341, 4,201,836, 4,272,32, 4,294,672, 4,301,229, 4,396,468, 4,427,500, 4,468,295, 4,476,006, 4,482,434, 4,545,875, 4,548,683, 4,564,429, 4,581,996, 4,618,405, 4,735,696, 4,897,168 and 4,919,774.

[0031]

As the anodization to be conducted after graining there is practiced anodization with an acid such as sulfuric acid and phosphoric acid. The anodization is preferably followed by surface hydrophilicization such as thermal silication and electric silication.

[0032]

In the anodization, it is preferred that an anodized layer be formed on the surface of the aluminum sheet in an amount of 0.3 g/m<sup>2</sup> or more, particularly from 0.5 to 10 g/m<sup>2</sup>. The anodized layer is porous. The diameter of these pores depends on the anodization conditions and can fall within a wide range

but normally is from about 5 to 1,000 angstrom, preferably from 10 to 500 angstrom.

[0033]

The surface hydrophilicization of the aluminum sheet by anodization and silication has been already known widely.

[0034]

Examples of patents concerning the anodization of lithographic printing plate precursors include US Patents 2,594,289, 2,703,781, 3,227,639, 3,511,661, 3,804,731, 3,915,811, 3,988,217, 4,022,670, 4,115,211, 4,229,266 and 4,647,346.

[0035]

As the coating material to be used in the surface hydrophilicization there may be used a polyvinylphosphonic acid, polyacrylic acid, polyacrylamide, zirconate or titanate besides the aforementioned silicate. Examples of patents concerning the surface hydrophilicization include US Patents 2,714,066, 3,181,461, 3,220,832, 3,265,504, 3,276,868, 3,549,365, 4,090,880, 4,153,461, 4,376,914, 4,383,987, 4,399,021, 4,427,765, 4,427,766, 4,448,647, 4,452,674, 4,458,005, 4,492,616, 4,578,156, 4,689,272 and 4,935,332, and European Patent 190,643.

[0036]

The thickness of the hydrophilicized aluminum sheet thus obtained is preferably from 0.1 to 1 mm, more preferably from

0.15 to 0.5 mm, particularly from 0.15 to 0.4 mm.

[0037]

In order to provide a hydrophilic polymer layer on the aforementioned various supports (2), the hydrophilic polymer layer may comprise a hydrophilic binder polymer optionally cured with a crosslinking agent or the like incorporated therein in an amount of from 5 to 100% by weight, preferably from 20 to 95% by weight, more preferably from 40 to 90% by weight based on the total solid content in the hydrophilic polymer layer to keep itself hydrophilic.

[0038]

The hydrophilic binder polymer to be used herein is a networked polymer formed by carbon-carbon bonds having as side chain one or a plurality of hydrophilic functional groups such as carboxyl group, amino group, phosphoric acid group, sulfonic acid group, salt thereof, hydroxyl group, amide group and polyoxyethylene group, a polymer having any of carbon atom and carbon-carbon atom bonded thereto via heteroatom formed by at least one oxygen, nitrogen, sulfur and phosphorus or a polymer having as side chain one or a plurality of hydrophilic functional groups such as carboxyl group, amino group, phosphoric acid group, sulfonic acid group, salt thereof, hydroxyl group, amide group and polyoxyethylene group. Specific examples of these polymers include poly(meth)acrylate-based polymers, polyoxyalkylene-based polymers, polyurethane-based polymers,

epoxy ring-opening addition polymer-based polymers, poly(meth)acrylic acid-based polymers, poly(meth)acrylamide-based polymers, polyester-based polymers, polyamide-based polymers, polyamine-based polymers, polyvinyl-based polymers, polysaccharide-based polymers, and cellulose derivative-based polymers. Preferred among these polymers are those having as segment side chain one or a repetition of combination of two or more of hydroxyl group, carboxyl group, alkaline metal salt thereof, amino group, halogenated hydrogen salt thereof, sulfonic acid and amine salt, alkaline metal salt and alkaline earth metal salt thereof and amide and those having these hydrophilic functional groups and a polyoxyethylene group overlapped on part of the main chain segment because they have a high hydrophilicity. Even more desirable among these polymers are those having a urethane bond or urea bond in the main chain or side chain of hydrophilic binder polymer because they are excellent not only in hydrophilicity but also in press life of non-image area.

[0039]

The hydrophilic polymer layer containing a hydrophilic binder polymer of the invention will be further described hereinafter. The term "(meth)acrylate" as used herein is meant to indicate "acrylate and/or methacrylate". The term "(meth)acryl" as used herein is meant to indicate "acryl and/or methacryl". Further, the hydrophilic binder polymer according

to the invention may comprise other various components incorporated therein as necessary.

[0040]

In order to form a hydrophilic polymer layer containing a hydrophilic binder polymer according to the invention, at least one selected from the group consisting of hydrophilic monomers having a hydrophilic group such as (meth)acrylic acid, alkaline and amine salts thereof, itaconic acid, alkaline and amine salts thereof, 2-hydroxyethyl (meth)acrylate, (meth)acrylamide, N-monomethylol (meth)acrylamide, N-dimethylol (meth)acrylamide, 3-vinylpropionic acid, alkaline and amine salts thereof, vinylsulfonic acid, alkaline and amine salts thereof, 2-sulfoethyl (meth)acrylate, polyoxyethylene glycol mono(meth)acrylate, 2-acrylamide-2-methylpropanesulfonic acid, acid phosphoxypolyoxyethylene glycol mono(meth)acrylate, allylamine, salt thereof with hydroxyl group such as halogenated hydroxyl, carboxyl group, salt thereof, sulfonic acid, salt thereof, phosphoric acid, salt thereof, amide group, amino group and ether group is used to synthesize a hydrophilic homopolymer or copolymer.

[0041]

The hydrophilic binder polymer having a functional group such as hydroxyl group, carboxyl group, amino group, salt thereof and epoxy group can be converted to an unsaturated

group-containing polymer having an ethylenically addition-polymerizable unsaturated group such as vinyl group, allyl group and (meth)acryl group or a ring-forming group such as cinnamoyl group, cinnamylidene group, cyanocinnamylidene group and p-phenylenediacrylate group incorporated therein by the use of these functional groups. If necessary, to the unsaturated group-containing polymer are added monofunctional and polyfunctional monomers copolymerizable with the unsaturated group, a polymerization initiator described later and other components described later. The mixture is then dissolved in a proper solvent to prepare a coating solution. The coating solution is spread over the support, and then subjected to three-dimensional crosslinking after or during drying.

[0042]

The hydrophilic binder polymer containing an active hydrogen such as hydroxyl group, amino group and carboxyl group is added to an active hydrogen-free solvent such as methyl ethyl ketone, propylene glycol monomethyl ether acetate and cyclohexanone with an isocyanate compound or blocked polyisocyanate compound and other components described later to prepare a coating solution. The coating solution thus prepared is spread over the support, and then subjected to three-dimensional crosslinking after or during drying.

[0043]



As the copolymerizable component of the hydrophilic binder polymer there may be used a monomer having a glycidyl group such as glycidyl (meth)acrylate or a carboxyl group such as (meth)acrylic acid as well. The glycidyl group-containing hydrophilic binder polymer comprising such a copolymerizable component can be subjected to three-dimensional crosslinking by the ring-opening reaction with an  $\alpha$ ,X-alkane or alkenedicarboxylic acid such as 1,2-ethanedicarboxylic acid and adipic acid, a polycarboxylic acid such as 1,2,3-propanetricarboxylic acid and trimellitic acid, a polyamine compound such as 1,2-ethanediamine, diethylenediamine, diethylenetriamine and  $\alpha$ ,X-bis-(3-aminopropyl)-polyethylene glycol ether, an oligoalkylene or polyalkylene glycol such as ethylene glycol, propylene glycol, diethylene glycol and tetraethylene glycol or a polyhydroxy compound such as trimethylolpropane, glycerin, pentaerythritol and sorbitol as a crosslinking agent.

[0044]

The hydrophilic binder polymer having a carboxyl group or amino group can be subjected to three-dimensional crosslinking by the epoxy ring-opening reaction with a polyepoxy compound such as ethylene glycol diglycidyl ether, propylene glycol diglycidyl ether, polyethylene glycol diglycidyl ether, polypropylene glycol diglycidyl ether, 1,6-hexanediol diglycidyl ether and trimethylolpropane triglycidyl ether as

a crosslinking agent.

[0045]

Polysaccharides such as cellulose derivative, polyvinyl alcohols, partial saponification products thereof, glycidol homopolymer, glycidol copolymer or hydrophilic binder polymers based thereon can be subjected to three-dimensional crosslinking in the aforementioned manner by introducing the aforementioned crosslinkable functional group using the hydroxyl group contained therein.

[0046]

A polymer having an ethylenically addition-polymerizable unsaturated group or ring-forming group incorporated in a hydrophilic polyurethane precursor synthesized from a polyol or polyamine terminated by a hydroxyl group or amino group such as polyoxyethylene glycol and a polyisocyanate such as 2,4-tolylenediisocyanate, 2,6-tolylenediisocyaante, 1,6-hexamethylenediisocyanate and isophoronediiisocyanate can be subjected to three-dimensional crosslinking in the aforementioned manner.

[0047]

In the case where the hydrophilic polyurethane precursor thus synthesized is terminated by an isocyanate group, it is reacted with a compound having an active hydrogen such as glycerol mono(meth)acrylate, 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, N-monomethylol

(meth)acrylamide, N-dimethylol (meth)acrylamide, (meth)acrylic acid, cinnamic acid and cinnamic acid alcohol. In the case where the hydrophilic polyurethane precursor thus synthesized is terminated by a hydroxyl group or amino group, it is reacted with (meth)acrylic acid, glycidyl (meth)acrylate, 2-isocyanatoethyl (meth)acrylate or the like.

[0048]

Further, a coat of a polybasic acid and a polyol or polyamine may be subjected to thermal three-dimensional crosslinking or a water-soluble colloid-forming compound such as casein, glue and gelatin may be subjected to thermal three-dimensional crosslinking to form a networked hydrophilic binder polymer.

[0049]

Moreover, a method may be used which comprises reacting a hydroxyl group or amino group-containing hydrophilic polymer such as homopolymer or copolymer synthesized from hydroxyl group-containing monomer (e.g., 2-hydroxyethyl (meth)acrylate, vinyl alcohol) or allylamine, partially saponified polyvinyl alcohol, polysaccharides (e.g., cellulose derivative), glycidol homopolymer and glycidol copolymer with a polybasic acid anhydride having two or more acid anhydride groups per molecule to form a three-dimensionally crosslinked hydrophilic binder polymer.

[0050]

Examples of the polybasic acid anhydrides employable herein include ethylene glycol bisanhydrotrimellitate, glycerol trisanhydrotrimellitate, 1,3,3a,4,5,9b-hexahydro-5-(tetrahydro-2,5-dioxo-3-furanyl)-naphtho[1,2-C]furane-1,3-dione, 3,3',4,4'-diphenylsulfonetetracarboxylic acid dianhydride, and 1,2,3,4-butanetetracarboxylic acid dianhydride.

[0051]

A solution or dispersion of an active hydrogen-containing compound such as polyurethane and polyamine or polyol having isocyanate group left at its terminal and other components described later in a solvent may be spread over a support, freed of the solvent, and then cured at a temperature such that the microcapsules cannot be destroyed to undergo three-dimensional crosslinking. In this case, the polymer may be rendered hydrophilic by introducing hydrophilic functional groups into the segment and side chain of either or both of polyurethane and active hydrogen-containing compound. As the segment or functional group for providing hydrophilicity there may be properly selected from the aforementioned groups.

[0052]

Examples of the polyisocyanate compounds employable herein include 2,4-tolylenediisocyanate, 2,6-tolylene diisocyanate, 4,4'-diphenylmethanediisocyanate, 1,5-naphthalenediisocyanate, tolidinediisocyanate, 1,6-

hexamethylenediisocyanate, isophoronediiisocyanate, xylyenediiisocyanate, lysinediiisocyanate, triphenylmethane triisocyanate, and bicycloheptanetriisocyanate.

[0053]

For the purpose of preventing the change of isocyanate group during handling before and after spreading, it is occasionally preferred that the isocyanate group be blocked (masked) by any known method. For this purpose, a masking agent such as acidic sodium sulfite, aromatic secondary amine, tertiary alcohol, amide, phenol, lactam, heterocyclic compound and ketoxim may be used according to Takaharu Iwata, "Prasutikku Zairyo Koza (2)-Poriuretan Jushi (Institute of Plastic Materials (2) - Polyurethane Resin)", Nikkan Kogyo Shinbunsha, 1974, pp. 51 - 52, Takaharu Iwata, "Poriuretan Jushi Handobukku (Handbook of Polyurethane Resins)", Nikkan Kogyo Shinbunsha, 1987, pages 98, 419, 423, 499, etc. Particularly preferred among these masking agents are those which have a low isocyanate regeneration temperature and are hydrophilic such as acidic sodium sulfite.

[0054]

The aforementioned non-blocked or blocked polyisocyanate may be provided with an addition-polymerizable unsaturated group so that it can be used for the enhancement of crosslinking or the reaction with lipophilic component. The degree of crosslinking such as interlinking average molecular weight

depends on the kind of the segment used and the kind and amount of the associatable functional group but may be determined according to the desired press life. In general, the interlinking average molecular weight is predetermined to fall within a range of from 500 to 50,000. When this value is shorter than 500, the resulting product tends to be brittle. On the contrary, when this value is longer than 50,000, the resulting product disadvantageously swells with a fountain solution and exhibits a deteriorated press life. From the standpoint of balance of press life and hydrophilicity, it is practical that the interlinking average molecular weight is from about 800 to 30,000, particularly from about 1,000 to 10,000.

[0055]

The hydrophilic binder polymer of the invention may be used in combination with the following monofunctional and polyfunctional monomers.

[0056]

Examples of these monofunctional and polyfunctional monomers include those disclosed in Sinzo Yuge and Tosuke Kaneko, "Kakyozei Handobukku (Handbook of Crosslinking Agents)", Taiseisha, 1981, Kiyomi Kato, "Shigaisen Koka Sisutemu (Ultraviolet Curing System)", General Technology Center, 1989, Kiyomi Kato, "UV-EB Koka Handobukku (Genryohen) (Handbook of UV-EB Curing) (Edition of material))", Kobunshi Kankokai, 1985, Kiyoshi Akamatsu, "Shin Kankosei Jushi no Jissai Gijutsu

(Practical Technique of Photosensitive Resins (revised)), CMC,  
 pp. 102 - 114, 1987, etc., i.e., N,N'-methylenebisacrylamide,  
 (meth)acryloylmorpholine, vinylpyridine,  
 N-methyl(meth)acrylamide, N,N-dimethyl(meth)acrylamide,  
 N,N-dimethylaminopropyl(meth)acrylamide,  
 N,N-dimethylaminoethyl(meth)acrylate, N,N-diethylamino  
 ethyl(meth)acrylate, N,N-dimethylaminoneopenthyl  
 (meth)acrylate, N-vinyl-2-pyrrolidone, diacetone acrylamide,  
 N-methylol(meth)acrylamide, parastyrenesulfonic acid and salt  
 thereof, methoxy triethylene glycol(meth)acrylate, methoxy  
 tetraethylene glycol(meth)acrylate (number-average molecular  
 weight of PEG: 400), methoxypolyethylene glycol(meth)acrylate  
 (number-average molecular weight of PEG: 1,000), butoxyethyl  
 (meth)acrylate, phenoxyethyl(meth)acrylate, phenoxy  
 diethylene glycol(meth)acrylate, nonylphenoxyethyl  
 (meth)acrylate, dimethylol tricyclodecane di(meth)acrylate,  
 polyethylene glycol di(meth)acrylate (number-average  
 molecular weight of PEG: 400), polyethylene glycol  
 di(meth)acrylate (number-average molecular weight of PEG: 600),  
 polyethylene glycol di(meth)acrylate (number-average  
 molecular weight of PEG: 1,000), polypropylene glycol  
 di(meth)acrylate (number-average molecular weight of PEG: 400),  
 2,2-bis[4-(methacryloxyethoxy)phenyl]propane,  
 2,2-bis[4-methacryloxy-diethoxy)phenyl]propane, 2,2-bis[4  
 -methacryloxy-polyethoxy)phenyl]propane, acrylation product

thereof,  $\beta$ -(meth)acryloyloxyethylhydrogen phthalate,  $\beta$ -(meth)acryloyloxyethylhydrogen succinate, polyethylene glycol mono(meth)acrylate, polyphenylene glycol mono(meth)acrylate, 3-chloro-2-hydroxypropyl (meth)acrylate, 1,3-butyleneglycol di(meth)acrylate, 1,6-hexanediol di(meth)acrylate, 1,6-hexanediol di(meth)acrylate, neopentylglycol di(meth)acrylate, trimethylolpropane tri(meth)acrylate, tetramethylolpropane tri(meth)acrylate, tetramethylolpropane tetra(meth)acrylate, isobornyl (meth)acrylate, lauryl (meth)acrylate, tridecyl (meth)acrylate, stearyl (meth)acrylate, isodecyl (meth)acrylate, cyclohexyl (meth)acrylate, tetrafurfuryl (meth)acrylate, benzyl (meth)acrylate, mono(2-acryloyloxyethyl)acid phosphate, methacrylation product thereof, glycerin mono(meth)acrylate, glycerin di(meth)acrylate, tris(2-acryloyloxyethyl)isocyanurate, methacrylation product thereof, N-phenylmaleimide, N-(meth)acryloxysuccinic acid imide, N-vinylcarbazole, divinylethylenurea, and divinylpropyleneurea.

[0057]

Further, the hydrophilic polymer layer to be used in the invention may comprise a colloidal silica having a particle diameter of from 10 to 40 nm, a colloidal alumina having a particle diameter of from 10 to 100 nm, a carboxylic acid such as acetic acid, formic acid, citric acid, tartaric acid, malic acid and



itaconic acid and salt thereof, singly or in admixture thereof, incorporated therein in an amount of from 0 to 90% by weight, preferably from 0 to 80% by weight based on the total solid content in the hydrophilic polymer layer for the purpose of enhancing the retention of fountain solution.

[0058]

Moreover, the hydrophilic polymer layer may comprise a proper surface active agent incorporated therein in an amount of from 0.01 to 10% by weight based on the total solid content in the hydrophilic polymer layer coating solution for the purpose of enhancing the spreadability of the photosensitive layer.

[0059]

The thickness of the hydrophilic polymer layer to be used in the invention is from 0.1 to 100  $\mu\text{m}$ , preferably from 0.2 to 50  $\mu\text{m}$ , more preferably from 0.5 to 20  $\mu\text{m}$ . The thickness of the aforementioned various supports (2) having such a hydrophilic polymer layer is preferably from 25  $\mu\text{m}$  to 1 mm, particularly from 50 to 500  $\mu\text{m}$ , even more particularly from 50 to 300  $\mu\text{m}$ .

[0060]

The compound having at least one addition-polymerizable ethylenically double bond (hereinafter referred to as "ethylenic compound") to be incorporated in the photosensitive layer formed on the hydrophilic support in the invention will be further described hereinafter.

[0061]

This ethylenic compound is a monomer having an ethylenically unsaturated bond which undergoes addition polymerization and curing when acted on by a photopolymerization initiation system (The term "monomer" as used herein is meant to indicate a conception contrary to so-called polymer and thus includes dimer, trimer and oligomer besides monomer in a narrow sense). This ethylenic compound enters in the indentation or pores on the surface of the hydrophilic support so that when exposed to light, it is photo-set to enhance the adhesivity between the photosensitive layer and the hydrophilic support. At the same time, this ethylenic compound forms a photosensitive layer which is strong enough to resist the physical stimulation during printing. On the other hand, this ethylenic compound exhibits a relatively adhesivity to the hydrophilic support and a gummed tape peel strength as defined herein before curing. Accordingly, it is required that this ethylenic compound can be easily transferred to the surface of the blanket roller and removed from the hydrophilic support by the adhesivity of the printing ink during printing on the unexposed area of the photosensitive layer so that the hydrophilic surface of the support can be exposed.

[0062]

Further, this ethylenic compound is required to be capable of providing the unexposed photosensitive layer with a gummed

tape peel strength of 150 g/cm or more, preferably greater than 200 g/cm from the unexposed area of the support of the photo-set photosensitive layer when exposed to light wherein the unexposed photosensitive layer has a gummed tape peel strength of from 0.5 to 200 g/cm, preferably from 1 to 150 g/cm, more preferably from 2 to 100 g/cm, even more preferably from 10 to 100 g/cm when peeled off from the hydrophilic support.

[0063]

When the gummed tape peel strength of the aforementioned unexposed photosensitive layer is remarkably low, the photosensitive layer is peeled off from the hydrophilic support during the handling of the photosensitive lithographic printing plate precursor. On the contrary, when the gummed tape peel strength of the aforementioned unexposed photosensitive layer is remarkably high, malclearing (remaining of non-image area) occurs during development.

[0064]

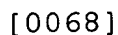
Further, when the peel strength of the hydrophilic support on the exposed area is remarkably low, the resulting printing plate exhibits a lowered sensitivity. On the contrary, when the peel strength of the hydrophilic support on the exposed area is remarkably high, no photo-set image can be formed.

[0065]

Accordingly, in the invention, as ethylenic compounds there are preferably used an ethylenic compound having a urethane

[0066]

[0067]



36

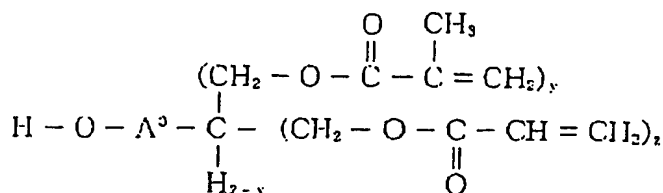
of from 0 to 3, with the proviso that x, y and z satisfy the equation  $y + z - x = 1$ ; and  $A^3$  represents an alkylene group having from 1 to 3 carbon atoms or a direct bond.

As the compound having a partial structure represented by the general formula (I) there may be normally used a urethane compound obtained by the reaction of an organic diisocyanate compound or trimer thereof with a (meth)acryloyl group-containing hydroxy compound.

[0069]

Examples of the organic diisocyanate compound employable herein include aliphatic diisocyanates such as hexamethylene diisocyanate and trimethylhexamethylene diisocyanate, alicyclic diisocyanates such as cyclohexane diisocyanate and isophorone diisocyanate, and aromatic diisocyanates such as tolylene diisocyanate and diphenylmethane diisocyanate. Examples of the (meth)acryloyl group-containing hydroxy compound to be reacted with the organic diisocyanate compound or trimer thereof include those represented by the following general formula (II).

[0070]



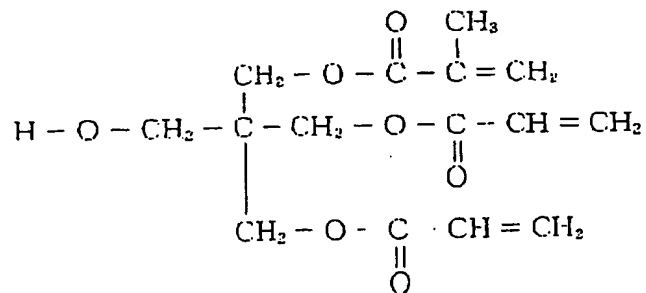
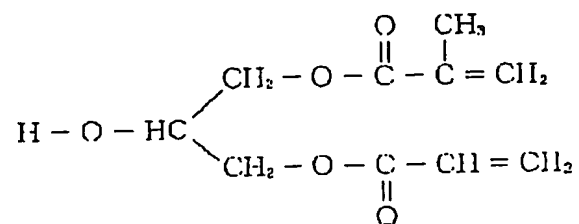
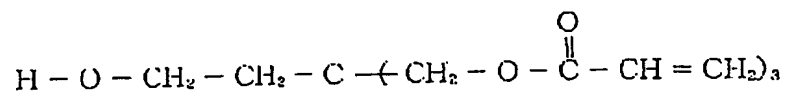
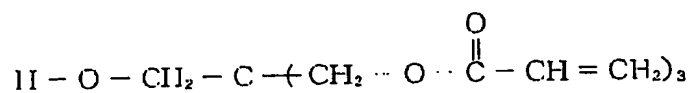
(II)

[0071]

wherein x, z, y and A<sup>3</sup> are as defined in the general formula (I).

Examples of the (meth)acryloyl group-containing hydroxy compound employable herein include the following compounds:

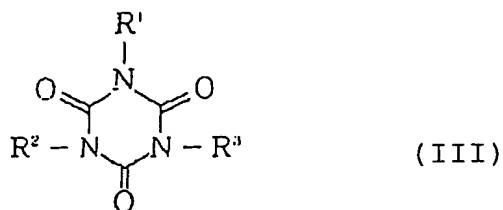
[0072]



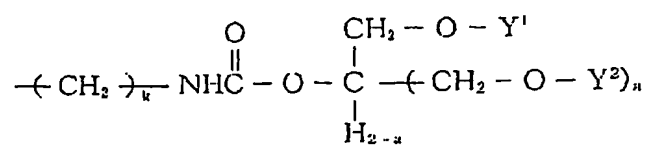
[0073]

Representative examples of the urethane compound obtained by the reaction of the aforementioned organic diisocyanate compound or trimer thereof with the (meth)acryloyl group-containing hydroxy compound include those represented by the following general formulae (III) to (VI).

[0074]

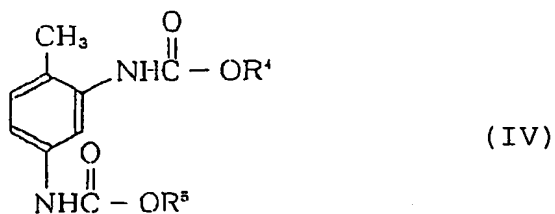


wherein  $\text{R}^1$  to  $\text{R}^4$  each independently represent a group represented by the following general formula:

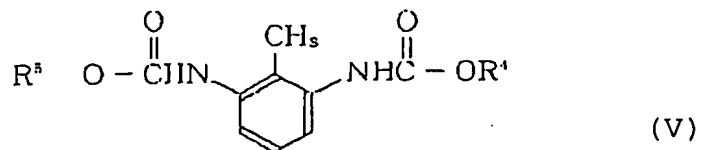


wherein  $k$  represents an integer of from 1 to 10, preferably from 5 to 7;  $a$  represents an integer of 1 or 2; and  $\text{Y}^1$  and  $\text{Y}^2$  each independently represent an acryloyl group or methacryloyl group.

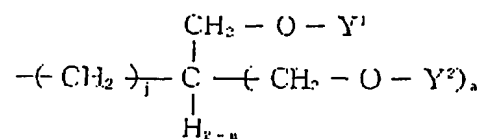
[0075]





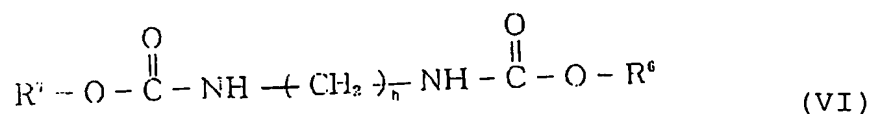


wherein  $\text{R}^4$  and  $\text{R}^5$  each independently represent a group represented by the following general formula:

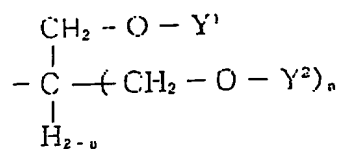


wherein  $j$  represents an integer of from 1 to 3, preferably 1 or 2;  $a$  represents an integer of 1 or 2; and  $\text{Y}^1$  and  $\text{Y}^2$  each independently represent an acryloyl group or methacryloyl group.

[0076]



wherein  $h$  represents an integer of from 1 to 10, preferably from 5 to 7; and  $\text{R}^6$  and  $\text{R}^7$  each independently represent a group represented by the following general formula:



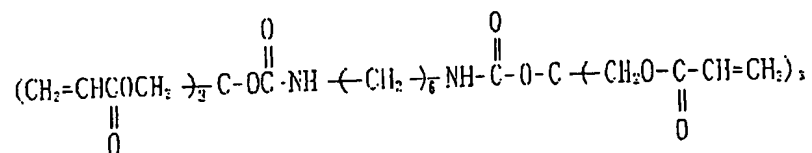
wherein a represents an integer of from 1 or 2; and Y<sup>1</sup> and Y<sup>2</sup> each independently represent an acryloyl group or methacryloyl group.

[0077]

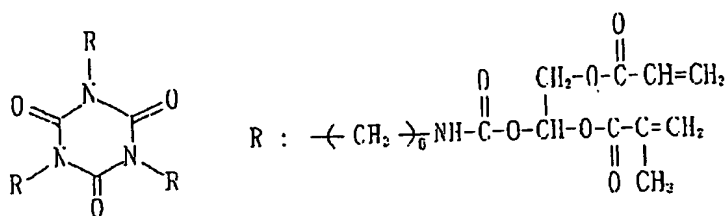
Preferred examples of the ethylenic compound having a urethane skeleton to be used in the invention include the following compounds E-1 to E-11.

[0078]

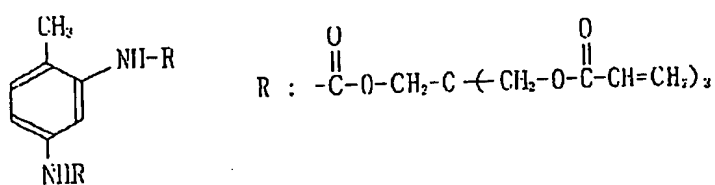
E - 1



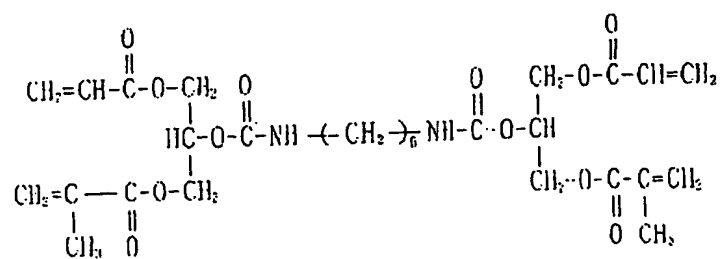
E - 2



E - 3

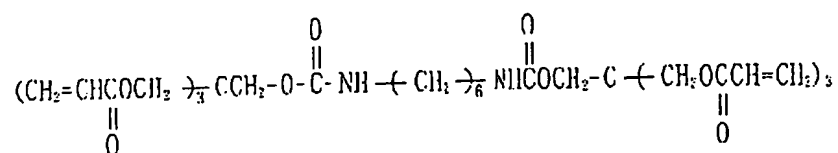


E - 4

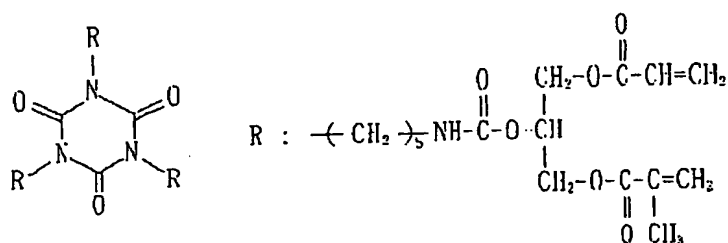


[0079]

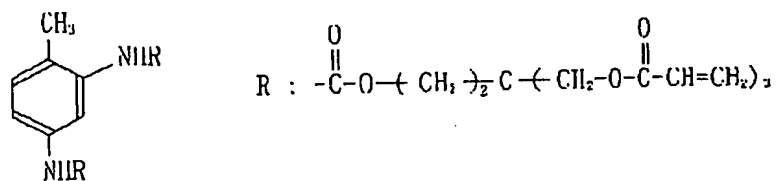
E - 5



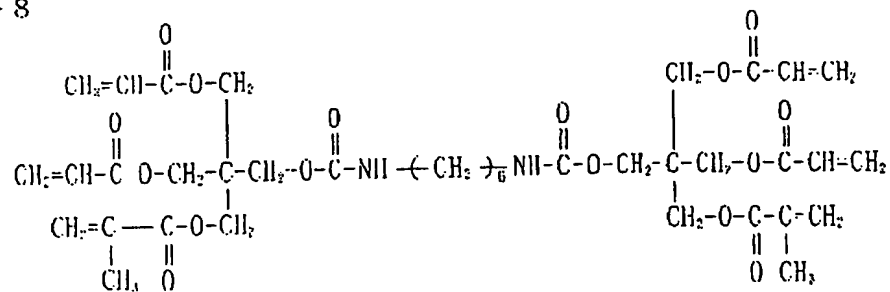
E - 6



E - 7



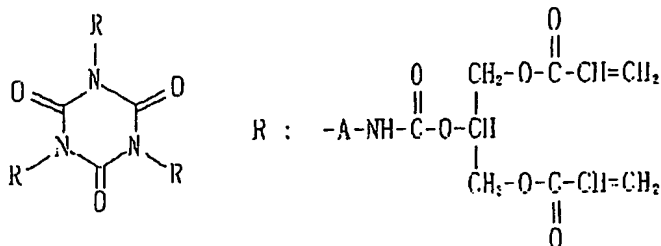
E - 8





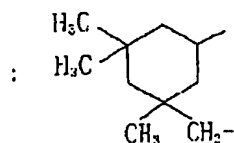
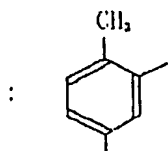
[0081]

E-11



wherein A represents any one of the following groups; and the three substituents R are the same.

A:  $: \text{---}(\text{CH}_2)_6\text{---}$



[0082]

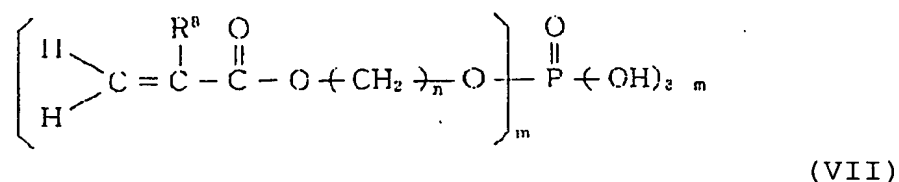
These ethylenic compounds having a urethane skeleton are normally used singly or in admixture of two or more thereof in an amount of from 10 to 90% by weight, preferably from 20 to 70% by weight based on the total solid content in the photosensitive layer. When the mixing proportion of the ethylenic compounds falls below 10% by weight, the resulting printing plate exhibits a deteriorated press life. On the contrary, when the mixing proportion of the ethylenic compounds

exceeds 90% by weight, the transferability of the unexposed photosensitive layer to the blanket roller can be easily deteriorated. Thus, troubles occur in any case.

[0083]

Among these specific ethylenic compounds, the ester of (meth)acryloyl group-containing compound with phosphoric acid is not specifically limited so far as it is an ester of phosphoric acid with a (meth)acryloyl group-containing compound. Specific examples of such an ester compound include compounds represented by the following general formula (VII). Such a compound is useful to enhance the sensitivity and press life of the printing plate as well as the transferability of the unexposed area to the blanket roller during printing.

[0084]



wherein  $R^8$  represents a hydrogen atom or methyl group;  $n$  represents an integer of from 1 to 25; and  $m$  represents an integer of from 1 or 2.

[0085]

Preferred among the compounds represented by the general formula (VII) are those having an integer of from 1 to 10 from the standpoint of improvement of press life and clearability of non-image area. Preferred examples of the compound represented by the general formula (VII) include methacryloxyethyl phosphate, and bis(methacryloylethyl) phosphate.

[0086]

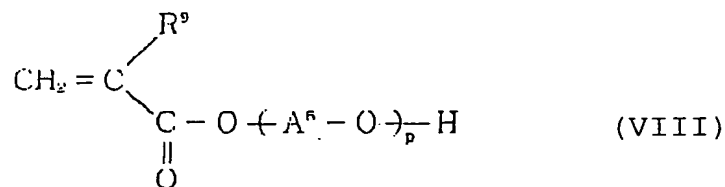
These phosphoric acid ester compounds are normally used singly or in admixture of two or more thereof in an amount of from 0.1 to 30% by weight, preferably from 0.2 to 25% by weight based on the total solid content in the photosensitive layer. When the mixing proportion of the phosphoric acid ester compounds falls below 0.1% by weight, the adhesivity to the support and the transferability to the unexposed photosensitive layer are deteriorated. On the contrary, when the mixing proportion of the phosphoric acid ester compounds exceeds 30% by weight, the resulting printing plate precursor exhibits a deteriorated sensitivity.

[0087]

The hydroxy(mono/or poly)alkyleneoxy(meth)acrylate as specific ethylenic compound is capable of enhancing adhesivity, sensitivity and transferability of unexposed photosensitive layer and preferably has a structure represented by the following general formula (VIII):



[0088]



[0089]

wherein  $\text{R}^9$  represents a hydrogen atom or methyl group;  $\text{A}^6$  represents a  $\text{C}_1$ - $\text{C}_6$  alkylene group which may be substituted and branched; and  $p$  represents an integer of 2 or more.

In the general formula (VIII),  $\text{A}^6$  is preferably a  $\text{C}_2$ - $\text{C}_4$  alkylene group which may be substituted and branched. When the alkylene group is substituted by a halogen, the substituent is preferably a chlorine atom. More preferably,  $\text{A}^6$  is an unsubstituted  $\text{C}_2$ - $\text{C}_3$  alkylene group which may be branched, i.e., polyethylene glycol mono(meth)acrylate or polypropylene glycol mono(meth)acrylate. In the general formula (VIII),  $p$  may be an integer of 2 or more. In particular,  $p$  is preferably from 5 to 50 because there occurs best balanced adhesivity to support, sensitivity and developability.

[0090]

These hydroxy(mono/or poly) alkyleneoxy (meth)acrylates may be used singly or in admixture of two or more thereof. The content of these hydroxy(mono/or poly) alkyleneoxy

(meth)acrylates is not specifically limited but is normally from 0.1 to 30% by weight, preferably from 0.2 to 25% by weight, more preferably from 0.3 to 20% by weight based on the total solid content in the photosensitive layer. When the mixing proportion of these hydroxy(mono/or poly) alkyleneoxy (meth)acrylates falls below 0.1% by weight, the adhesivity to the support and the transferability of the unexposed photosensitive layer are deteriorated. On the contrary, when the mixing proportion of these hydroxy(mono/or poly) alkyleneoxy (meth)acrylates exceeds 30% by weight, the resulting printing plate precursor tends to have a deteriorated sensitivity.

[0091]

Referring to the aforementioned ester of (meth)acryloyl group-containing compound with phosphoric acid and the aforementioned hydroxy(mono/or poly) alkyleneoxy (meth)acrylate compound as specific ethylenic compounds, the ester of (meth)acryloyl group-containing compound with phosphoric acid is preferably applied to an aluminum sheet which has not been subjected to hydrophilicization with silicic acid but has been merely subjected to graining and anodization as a hydrophilic support to perform various functions effectively. The hydroxy(mono/or poly) alkyleneoxy (meth)acrylate compound is preferably applied to a grained and anodized aluminum sheet which has been subjected to hydrophilicization with silicic

acid as a hydrophilic support.

[0092]

In the invention, ethylenic compounds other than the aforementioned ethylenic compounds may be used as well. In particular, the aforementioned ethylenic compounds are preferably used in combination with a polyfunctional ethylenic compound having two or more ethylenic double bonds.

[0093]

Examples of such a polyfunctional ethylenic compound include ester of aliphatic polyhydroxy compound with unsaturated carboxylic acid, ester of aromatic polyhydroxy compound with unsaturated carboxylic acid, and ester obtained by esterification reaction of a polyvalent hydroxy compound such as aliphatic polyhydroxy compound and aromatic polyhydroxy compound with an unsaturated carboxylic acid and a polyvalent carboxylic acid.

[0094]

The ester of aliphatic polyhydroxy compound with unsaturated carboxylic acid is not specifically limited. Examples of the ester of aliphatic polyhydroxy compound with unsaturated carboxylic acid include acrylic acid ester of aliphatic polyhydroxy compound such as ethylene glycol diacrylate, triethyleneglycol diacrylate, trimethylolpropane triacrylate, trimethylolethane triacrylate, pentaerythritol triacrylate, pentaeryththritol tetraacrylate,

dipentaerythritol tetraacrylate, dipentaerythritol pentaacrylate and glycerol acrylate, methacrylic acid esters obtained by replacing the acrylate in these exemplified compounds by methacrylate, itaconic acid esters obtained by replacing the acrylate in these exemplified compounds by itaconate, crotonic acid esters obtained by replacing the acrylate in these exemplified compounds by crotonate, and maleic acid esters obtained by replacing the acrylate in these exemplified compounds by maleate.

[0095]

Examples of the ester of aromatic polyhydroxy compound with unsaturated carboxylic acid include acrylic acid ester and methacrylic acid ester of aromatic polyhydroxy compound such as hydroquinone diacrylate, hydroquinone dimethacrylate, resorcin diacrylate, resorcin dimethacrylate and pyrogallol triacrylate.

[0096]

The esterification reaction of an unsaturated carboxylic acid with a polyvalent carboxylic acid and a polyvalent hydroxy compound doesn't necessarily give a single compound. Representative examples of such an ester include condensates of acrylic acid, phthalic acid and ethylene glycol, condensates of acrylic acid, maleic acid and diethylene glycol, condensates of methacrylic acid, terephthalic acid and pentaerythritol, and condensates of acrylic acid, adipic acid, butanediol and

glycerin.

[0097]

Useful examples of the polyfunctional ethylenic compound to be used in the invention include epoxy acrylates such as adduct of diepoxy compound with hydroxyethyl acrylate, acrylamides such as ethylene bisacrylamide, allyl esters such as phthalic acid diallyl, and vinyl group-containing compounds such as divinyl phthalate.

[0098]

Examples of polymers having an ethylenic double bond in its main chain among these ethylenic compounds include polyester obtained by the polycondensation of unsaturated divalent carboxylic acid with dihydroxy compound, and polyamide obtained by the polycondensation of unsaturated didivalent carboxylic acid with diamine. Examples of the polymer having an ethylenic double bond in its side chain include divalent carboxylic acids having a double bond in its side chain such as polycondensate of itaconic acid, propyridenesuccinic acid or ethylidenemalonic acid with dihydroxy compound or diamine compound. Further, a polymer having a functional group having a reactivity such as hydroxyl group and halogenated methyl group in its side chain, e.g., polymer obtained by the polymerization reaction of polyvinyl alcohol, poly(2-hydroxyethylmethacrylate) or polyepichlorohydrin with acrylic acid, methacrylic acid or crotonic acid can be preferably

used.

[0099]

The mixing proportion of such an ethylenic compound is preferably from 5 to 98% by weight, particularly from 20 to 80% by weight, even more particularly from 20 to 70% by weight based on the total solid content in the photosensitive layer.

[0100]

The photopolymerization initiation system to be incorporated in the photosensitive layer according to the invention will be described hereinafter.

[0101]

As the photopolymerization initiation system there may be used any material capable of initiating the polymerization of the aforementioned ethylenic compound. Particularly preferred among these compounds are those sensitive to light in the range of from ultraviolet to near infrared.

[0102]

Examples of the photopolymerization initiation system which absorbs ultraviolet rays to generate radicals in the invention include dialkylacetophenone-based compounds, benzyldialkylketal-based compounds, benzoin-based compounds, benzoinalkylether-based compounds, thioxanthone derivatives and acylphosphine oxide-based compounds as disclosed in "Fine Chemical", Vol. 20, No. 4, March 1, 1991, pp. 16 - 26, hexaarylbiimidazole-based compounds and

s-trihalomethyltriazine-based compounds as disclosed in JP-A-58-40302 and JP-B-45-37377, and titanocene-based compounds as disclosed in JP-A-59-152396.

[0103]

Examples of the photopolymerization initiation system sensitive to light in the range of ultraviolet to visible light of 550 nm include system comprising hexaarylbiimidazole, radical generator and dye (as disclosed in JP-B-45-37377), system comprising hexaacrylbiimidazole and (p-dialkylaminobenzylidene)ketone (as disclosed in JP-A-47-2528 and JP-A-54-155292), system comprising substituted triazine and melocyanine dye (as disclosed in JP-A-54-451024), system comprising ketocoumarine and active agent (as disclosed in JP-A-52-142681, JP-A-58-15503, and JP-A-60-88005), system comprising substituted triazine and sensitizer (as disclosed in JP-A-58-29803 and JP-A-58-40302), system comprising biimidazole, styrene derivative and thiol (as disclosed in JP-A-59-56403), system comprising sensitizer containing dialkylaminophenol and biimidazole (as disclosed in JP-A-2-69, JP-A-57-168088, JP-A-5-107761, JP-A-5-210240, JP-A-4-288818), system comprising organic peroxide and dye (as disclosed in JP-A-59-140203 and JP-A-59-152396), titanocene system (as disclosed in JP-A-59-152396, JP-A-61-151197, JP-A-63-10602, JP-A-63-41484, JP-A-2-291, JP-A-3-12403, JP-A-3-20293, JP-A-3-27393 and JP-A-3-52050), and system

comprising titanocene, xanthene dye and addition-polymerizable ethylenically unsaturated double bond-containing compound having amino group or urethane group (as disclosed in JP-A-4-221958 and JP-A-4-219756).

[0104]

Preferred examples of the photopolymerization initiator sensitive to light in the range of from ultraviolet to light of 550 nm include composite photopolymerization initiator comprising a sensitizing dye having absorption in the wavelength range of from 400 to 500 nm, hexaarylbiimidazole such as 2,2'-bis(o-chlorophenyl)-4,4',5,5'-tetraphenylbiimidazole, 2,2'-bis(o-chlorophenyl)-4,4',5,5'-tetra(p-carboethoxyphenyl)biimidazole, 2,2'-bis(o-chlorophenyl)-4,4',5,5'-tetra(p-bromophenyl)biimidazole and 2,2'-bis(o-chlorophenyl)-4,4',5,5'-tetra(o,p-dichlorophenyl)biimidazole and organic thiol compound such as 2-mercaptobenzthiazole, 2-mercaptobenzoxazole and 2-mercaptobenzimidazole, and composite photopolymerization initiator comprising a sensitizing dye having absorption in the wavelength range of from 400 to 500 nm, a titanocene compound such as dicyclopentadienyl-Ti-bis-2,6-difluoro-3-(pyrrole-1-yl)-phenyl-1-yl, dicyclopentadienyl-Ti-bis-2,3,5,6-tetrafluorophenyl-1-yl and di-cyclopentadienyl-Ti-bis-2,3,4,5,6-pentafluorophenyl-1-yl and a dialkylaminophenyl compound such as p-diethylaminobenzoic acid



ethyl and Michler's ketone.

[0105]

Examples of the aforementioned dye for sensitizing hexabiimidazole include sensitizing dyes as disclosed in JP-A-2-69, JP-A-57-168088, JP-A-5-107761, JP-A-5-210240, and JP-A-6-116313.

[0106]

Examples of the dye for sensitizing titanocene include sensitizing dyes as disclosed in JP-A-6-295061, JP-A-6-301208, JP-A-7-219223, JP-A-7-281434, and JP-A-8-6245.

[0107]

Examples of the photopolymerization initiation system sensitive to light in the range of from visible light of 550 nm to near infrared include system comprising substituted triazine and squarium salt dye (as disclosed in JP-B-8-20734 and JP-A-2-306247), system comprising substituted triazine and cyanine dye (as disclosed in JP-A-2-189548), and system comprising azinium compound and cyanine dye or squarium salt dye (as disclosed in JP-A-63-142346).

[0108]

The mixing proportion of such a photopolymerization initiator is preferably from 0.1 to 50% by weight, particularly from 0.2 to 40% by weight, even more particularly from 0.5 to 30% by weight based on the total solid content in the photosensitive layer.

[0109]

The photopolymerization initiation system preferably comprises a sensitizer and an active agent incorporated therein in an amount of from 0.01 to 20% by weight and from 0.1 to 80% by weight, particularly from 0.05 to 10% by weight and from 0.5 to 50% by weight, respectively.

[0110]

The photosensitive layer according to the invention preferably comprises an organic polymer material (hereinafter referred to as "polymer binder") incorporated therein as a binder besides the aforementioned ethylenic compound and photopolymerization initiation system to modify the photosensitive layer and improve the physical properties of the photo-set photosensitive layer.

[0111]

In this case, the polymer binder to be used herein may be selected depending on compatibility, film-forming properties, adhesivity or properties to be improved.

[0112]

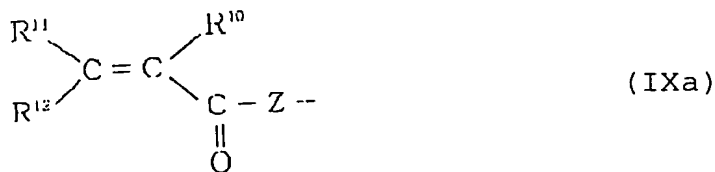
Specific examples of the polymer binder employable herein include homopolymers and copolymers of (meth)acrylic acid, (meth)acrylic acid ester, (meth)acrylamide, maleic acid, (meth)acrylonitrile, styrene, vinyl acetate, vinylidene chloride, maleimide, etc., polyethylene oxide, polyvinyl pyrrolidone, polyamide, polyurethane, polyester, polyether,

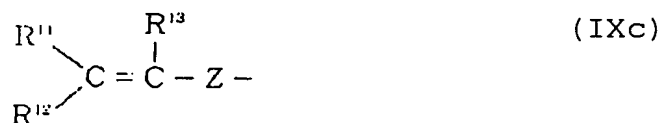
polyethylene terephthalate, acetyl cellulose, and polyvinyl butyral. Preferred among these polymer binders is a copolymer comprising at least one (meth)acrylic acid ester and a (meth)acrylic acid as copolymerizing components. The polymer binder having a carboxyl group in its molecule preferably has an acid value of from 10 to 250 and a weight-average molecular weight (hereinafter referred to as "Mw") of from 5,000 to 500,000.

[0113]

These polymer binders preferably have in its side chain an unsaturated bond, particularly at least one unsaturated bond represented by any one of the following general formulae (IXa) to (IXc):

[0114]





[0115]

wherein R<sup>10</sup> represents a hydrogen atom or methyl group; R<sup>11</sup> to R<sup>15</sup> each independently represent a hydrogen atom, halogen atom, amino group, dialkylamino group, carboxyl group, alkoxycarbonyl group, sulfo group, nitro group, cyano group, alkyl group which may have substituents, alkoxy group which may have substituents, aryloxy group which may have substituents, alkylamino group which may have substituents, arylamino group which may have substituents, alkylsulfonyl group which may have substituents or arylsulfonyl group which may have substituents; and Z represents an oxygen atom, sulfur atom, imino group or alkylimino group.

The substituents on the aforementioned alkyl group which may have substituents and other groups which may have substituents are not specifically limited so far as they don't extremely deteriorate the reactivity of carbon-carbon double bond but are normally selected from the group consisting of halogen atom, alkyl group, phenyl group, cyano group, nitro group, alkoxy group, alkylthio group and dialkylamino group.

[0116]

Preferred among the polymer binders represented by the general formula (IXa) are those wherein  $R^{10}$  is a hydrogen atom or methyl group and  $R^{11}$  and  $R^{12}$  each independently are a hydrogen atom, lower alkyl group, alkoxy group, dialkylamino group or cyano group. Preferred among the polymer binders represented by the general formula (IXb) are those wherein  $R^{11}$  and  $R^{12}$  each independently are a hydrogen atom, halogen atom, lower alkyl group, carboxyl group, alkoxy carbonyl group or cyano group,  $R^{13}$  is a hydrogen atom, halogen atom, lower alkyl group, carboxyl group, alkoxy carbonyl group or cyano group, and  $R^{14}$  and  $R^{15}$  each independently are a hydrogen atom, halogen atom or lower alkyl group. Preferred among the polymer binders represented by the general formula (IXc) are those wherein  $R^{11}$ ,  $R^{12}$  and  $R^{13}$  each independently are a hydrogen atom, halogen atom, lower alkyl group, carboxyl group, alkoxy carbonyl group or cyano group. From the standpoint of ease of addition reaction of carbon-carbon double bond in the general formulae (IXa) to (IXc), the compound of the general formula (IXa) is even more preferably one wherein at least two of  $R^{10}$  to  $R^{12}$  are hydrogen atoms and the compounds of the general formulae (IXb) and (IXc) are even more preferably ones wherein at least two of  $R^{11}$  to  $R^{13}$  are hydrogen atoms.

[0117]

Methods for the synthesis of these compounds can be roughly divided into two groups.

[0118]

(Synthesis method 1)

Synthesis method which comprises reacting a solution of a polymer binder having a carboxyl group in its molecule in an inert organic solvent (e.g., alcohol-based solvent, ester-based solvent, aromatic hydrocarbon-based solvent, aliphatic hydrocarbon-based solvent) and an epoxy group-containing unsaturated compound at a temperature of from about 80°C to 120°C for about 1 to 50 hours.

[0119]

The mixing proportion of the carboxyl group to be reacted with the epoxy group-containing unsaturated compound is not specifically limited so far as the effect of the invention can be exerted but is preferably from 5 to 90 mol-%, more preferably from 20 to 80 mol-%, even more preferably from 30 to 70 mol-% based on the total amount of the carboxyl group. When the mixing proportion of the carboxyl group falls within the above defined range, the resulting printing plate precursor exhibits a good developability as well as a good adhesivity.

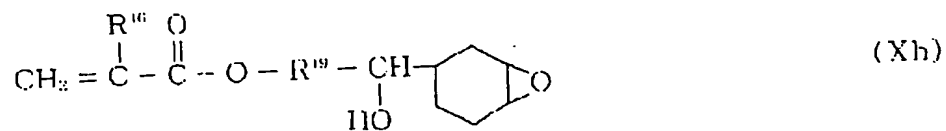
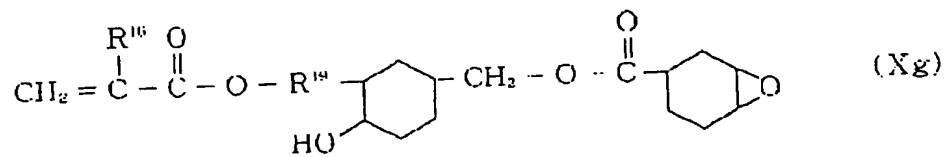
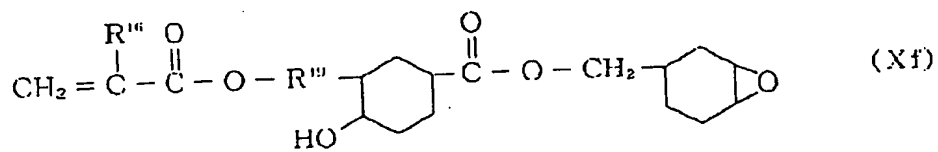
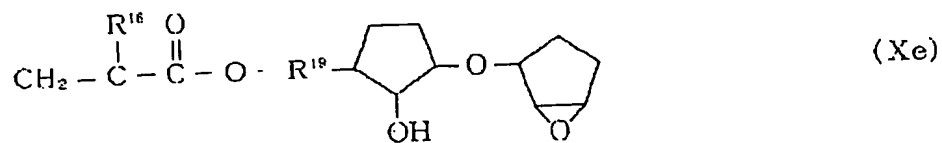
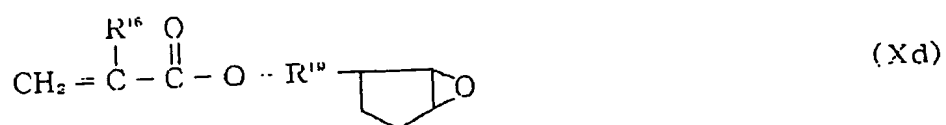
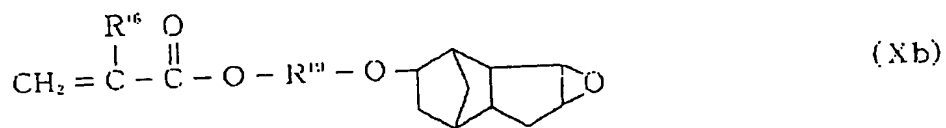
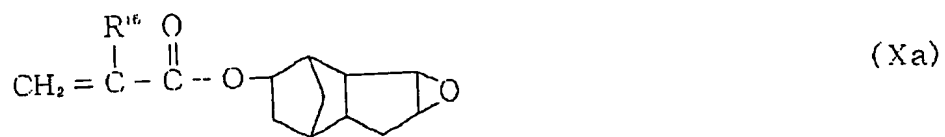
[0120]

The epoxy group-containing unsaturated compound to be used in the production of the ethylenic polymer binder having an unsaturated group in its side chain is a compound having at least one addition-polymerizable unsaturated bond and an epoxy group per molecule.

[0121]

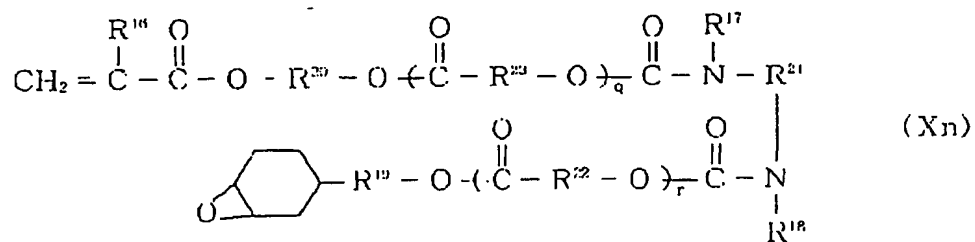
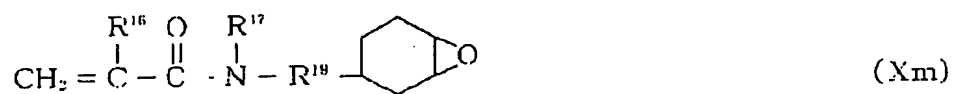
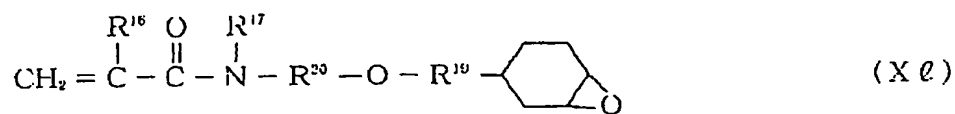
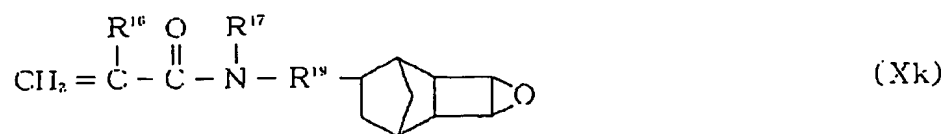
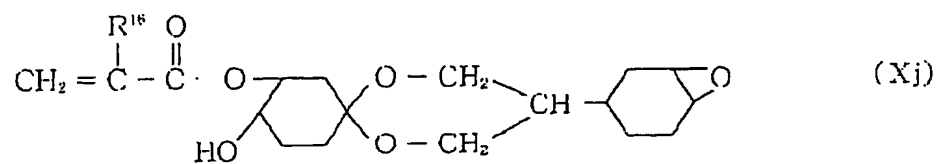
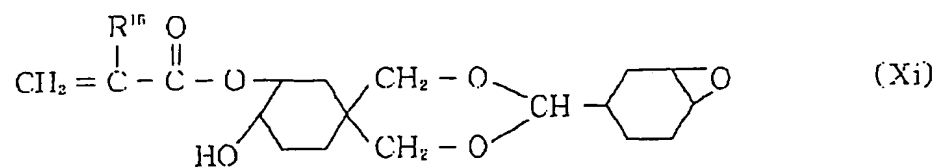
Examples of the epoxy group-containing unsaturated compound employable herein include aliphatic epoxy group-containing unsaturated compounds such as glycidyl (meth)acrylate, allylglycidylether,  $\alpha$ -ethylglycidylacrylate, crotonyl glycidyl ether, glycidyl crotonate, glycidyl isocrotonate, monoalkyl ester monoglycidyl ester itaconate, monoalkyl ester monoglycidyl ester fumarate and monoalkyl ester monoglycidyl ester maleate, and alicyclic epoxy group-containing unsaturated compounds represented by the following general formulae (Xa) to (Xn):

[0122]



[0123]





[0124]

wherein  $R^{16}$ ,  $R^{17}$  and  $R^{18}$  each independently represent a hydrogen atom or methyl group;  $R^{19}$ ,  $R^{20}$  and  $R^{21}$  each independently represent a  $C_1$ - $C_6$  divalent aliphatic saturated hydrocarbon group;  $R^{22}$  and  $R^{23}$  each independently represent a  $C_1$ - $C_{10}$  divalent hydrocarbon group; and  $q$  and  $r$  each represent an integer of from 0 to 10.

Specific examples of the aforementioned epoxy group-containing unsaturated compound include glycidyl methacrylate, allyl glycidyl ether, and 3,4-epoxycyclohexyl methyl acrylate. Particularly preferred among these epoxy group-containing unsaturated compounds are allyl glycidyl ether and 3,4-epoxycyclohexyl methyl acrylate.

[0125]

(Synthesis method 2)

Synthesis method involving the copolymerization of a compound having a total of two or more unsaturated bonds, including one or more unsaturated bonds having a low reactivity and one or more unsaturated bonds having a higher reactivity, represented by any one of the general formulae (IXb) and (IXc) with an unsaturated carboxylic acid.

[0126]

Specific examples of the compound having an unsaturated group represented by the general formula (IXb) employable herein include allyl (meth)acrylate, 3-allyloxyethyl (meth)acrylate, 3-allyloxy-2-hydroxypropyl (meth)acrylate, N,N-diallyl

(meth)acrylamide, cinnamyl (meth)acrylate, crotonyl (meth)acrylate, and methacryl (meth)acrylate. Particularly preferred among these compounds is allyl (meth)acrylate.

[0127]

Specific examples of the compound having an unsaturated group represented by the general formula (IXc) employable herein include vinyl (meth)acrylate, vinyl crotonate, 1-propenyl (meth)acrylate, 1-chlorovinyl (meth)acrylate, 2-phenylvinyl (meth)acrylate, and vinyl (meth)acrylate. Particularly preferred among these compounds is vinyl (meth)acrylate.

[0128]

The copolymerization of such a monomer with an unsaturated carboxylic acid, preferably acrylic acid or methacrylic acid, makes it possible to obtain the aforementioned copolymer having an unsaturated group. As the monomers to be copolymerized there may be used other monomers in addition to the unsaturated carboxylic acids. Examples of these monomers include acrylic acid alkyl, methacrylic acid alkyl, acrylonitrile, and styrene. The proportion of the compound having a structure of the general formula (IXb) or (IXc) to be copolymerized in the total amount of the polymer is preferably from 10 to 90 mol-%, more preferably from 30 to 80 mol-%. When this proportion falls below the above defined range, the resulting printing plate precursor exhibits deteriorated sensitivity and press life. On the contrary, when this proportion exceeds the above defined range, the resulting

printing plate precursor exhibits a deteriorated image reproducibility.

[0129]

The mixing proportion of such a polymer binder is preferably from 0 to 90% by weight, particularly from 20 to 80% by weight, even more particularly from 30 to 70% by weight based on the total solid content in the photosensitive layer.

[0130]

In order to form the photosensitive layer according to the invention from the aforementioned ethylenic compound, photopolymerization initiator and polymer binder, a photopolymerizable composition obtained by mixing these materials is spread over a proper hydrophilic support free from solvent or in the form of solution in a proper solvent, and then dried. Examples of the solvent, if used, include methyl ethyl ketone, cyclohexanone, butyl acetate, amyl acetate, ethyl propionate, toluene, xylene, monochlorobenzene, carbon tetrachloride, trichloroethylene, trichloroethane, dimethylformamide, methyl cellosolve, ethyl cellosolve, tetrahydrofuran, benzoquinone, propylene glycol monomethyl ether, and N-methylpyrrolidone. These solvents may be used singly or in admixture of two or more thereof.

[0131]

The photopolymerizable composition for forming the photosensitive layer may further comprise other additives such

as heat polymerization inhibitor (e.g., hydroquinone, p-methoxyphenol, 2,6-di-t-butyl-p-cresol), colorant made of organic or inorganic dye or pigment, plasticizer (e.g., dioctyl phthalate, didodecyl phthalate, tricresyl phosphate), sensitivity improver (e.g., tertiary amine, thiol) and other dye precursors incorporated therein as necessary.

[0132]

In this case, referring to preferred content of these various additives, the content of the heat polymerization inhibitor, the colorant such as dye and pigment, the plasticizer, the sensitivity improver and the dye precursor are 2% by weight or less, 40% by weight or less, 10% by weight or less, 20% by weight or less and 30% by weight or less based on the total solid content in the photosensitive layer, respectively.

[0133]

As the method for spreading the photopolymerizable composition over the hydrophilic support there may be used any known method such as dip coating method, rod coating method, spinner coating method, spray coating method and roll coating method. The photopolymerizable composition thus spread is then dried normally at a temperature of from 50°C to 150°C for 0.5 to 10 minutes.

[0134]

The photosensitive layer thus formed preferably stays nonadhesive at room temperature (25°C) and is in the form of

single layer type photosensitive lithographic printing plate precursor comprising only the photosensitive layer provided on a hydrophilic support free of protective layer on the photosensitive layer.

[0135]

However, a cover sheet may be provided on the photosensitive layer by lamination or spreading for the purpose of preventing the polymerization inhibition by oxygen or peeling and removing the unexposed area from the photosensitive layer as a pretreatment step of removing the unexposed area by the use of the adhesivity of the printing ink during printing.

[0136]

As such a cover sheet, if it is in the form of coating type oxygen barrier layer, there is preferably used one made of a water-soluble polymer such as polyvinyl alcohol, polyvinyl pyrrolidone, gelatin, polyethylene oxide, cellulose, water-soluble nylon, polyacrylic acid, polyacrylonitrile and starch, particularly polyvinyl alcohol. The thickness of the coat thus formed is normally from 0.2 to 10  $\mu\text{m}$ , preferably from 0.5 to 5  $\mu\text{m}$ , more preferably from 0.5 to 4  $\mu\text{m}$  because the desired oxygen barrier effect can be exerted when the thickness of the coat is 0.1  $\mu\text{m}$  or more. This thin film is peeled and removed with the unexposed photosensitive layer by the printing ink at the printing step after exposure.

[0137]

On the other hand, as the cover sheet capable of peeling and removing only the unexposed photosensitive layer from the support by the use of the adhesivity thereof to the photosensitive layer when peeled off from the support before printing there is preferably used one having a thickness great enough to resist the physical force applied thereto during the peeling of the aforementioned coating type oxygen barrier layer, e.g., from 1 to 100  $\mu\text{m}$ , preferably from 2 to 50  $\mu\text{m}$ , more preferably from 3 to 30  $\mu\text{m}$ .

[0138]

In the case where the cover sheet is provided by lamination, the cover sheet may be laminated on the photosensitive layer at a temperature such that the photosensitive layer becomes adhesive and peeled off from the photosensitive layer at room temperature.

[0139]

Examples of the material constituting such a cover sheet include polyesters such as polyethylene terephthalate, polyolefins such as polypropylene and polyethylene, various plastics such as cellophane, celluloid and polyvinyl alcohol, paper, cloth, wood, and metal such as aluminum. The thickness of the cover sheet is normally from 5 to 300  $\mu\text{m}$ , preferably from 5 to 150  $\mu\text{m}$ , more preferably from 10 to 100  $\mu\text{m}$ .

[0140]

Among these cover sheets, the transparent sheets can be

laminated on the photosensitive layer before or after imagewise exposure. However, the opaque sheets can be laminated on the photosensitive layer only after imagewise exposure.

[0141]

In general, the laminating cover sheet preferably has a proper oxygen barrier effect.

[0142]

In order to provide the cover sheet on the photosensitive layer by lamination, the photosensitive layer or the cover sheet may be coated with an adhesive layer for enhancing the adhesivity between the cover sheet and the photosensitive layer before lamination. In this arrangement, the cover sheet can be laminated on the photosensitive layer without using the adhesivity of the photosensitive layer, that is, at a lower temperature. In this case, it is preferred that such an adhesive layer be provided on the photosensitive layer so that the material of the adhesive layer enters in the indentation on the surface of the photosensitive layer to exert an anchoring effect that helps the unexposed photosensitive layer to be effectively peeled off.

[0143]

Examples of the material to be used in the formation of the adhesive layer include low softening emulsion type adhesives such as thermosetting urethane-based adhesive, epoxy-based adhesive and polyvinyl acetate, and non-curing normally



sticking adhesives. The thickness of the adhesive layer is normally from 0.1 to 100  $\mu\text{m}$ , preferably from 0.3 to 50  $\mu\text{m}$ , more preferably from 0.5 to 30  $\mu\text{m}$ .

[0144]

The aforementioned coating type cover sheet and laminating cover sheet may be used in combination to exhibit their capacities and characteristics in a proper combination.

[0145]

When the unexposed photosensitive layer is peeled off from the support by peeling the cover sheet, the photosensitive layer is preferably peeled and removed from the support in such a manner that only part of the unexposed photosensitive layer is peeled and removed while the remaining part of the photosensitive layer is left on the support. In this manner, the remaining photosensitive layer exerts an effect of protecting the hydrophilic surface of the support, making it possible to prevent the attachment of stain caused by contact with the conveyor roller or fingers during the conveyance of the sample. Further, the photosensitive layer left on the support is thin and permeable to oxygen. Thus, by remarkably lowering the photosensitivity of the remaining layer, an effect can be exerted of allowing the sample freed of cover sheet to be handled under daylight.

[0146]

The process for making a printing plate from the

print-developable light-sensitive lithographic printing plate precursor of the invention will be described hereinafter.

[0147]

The photosensitive lithographic printing plate precursor of the invention is subjected to imagewise exposure by a method involving contact exposure of the photosensitive lithographic printing plate precursor through a silver salt mask film for making printing plate disposed in close contact with the photosensitive layer or method involving the scanning exposure to light beam spot converged from a light source free from mask film so that the exposed photosensitive layer is photo-set.

[0148]

The exposure light source is not specifically limited but is particularly preferably carbon arc, high voltage mercury vapor lamp, xenon lamp, metal halide lamp, fluorescent lamp, tungsten lamp, halogen lamp, helium cadmium laser, argon ion laser, YAG laser, helium neon laser, laser having a wavelength of visible light to near infrared or the like.

[0149]

The photosensitive lithographic printing plate precursor which has been imagewise exposed to light can be mounted on the cylinder of the printing machine for printing. Shortly before the starting of printing, the adhesivity of the printing ink causes the unexposed photosensitive layer, which has a lower adhesivity to the hydrophilic support, to be peeled and removed

with the printing ink and transferred to the surface of the blanket rubber roller (cylinder). The photosensitive layer which has been transferred to the blanket rubber roller is then transferred to printing paper with the ink. Thus, the sheets of printing paper printed in the initial stage of printing are waste sheets, attaining printing development. In this arrangement, the hydrophilic surface of the support is exposed at this area. Accordingly, an image made of printing ink comprising balanced water and ink is formed on the surface of the printing plate. The ink image is transferred to the blanket roller from which is then transferred to printing paper to effect printing.

[0150]

Referring to another plate making process, the unexposed photosensitive layer of the photosensitive lithographic printing plate precursor which has been imagewise exposed to light may be peeled and removed before on-the-machine printing for the purpose of remarkably lowering the sensitivity of the unexposed area of the photosensitive lithographic printing plate precursor which has been exposed to light to allow the exposed photosensitive lithographic printing plate precursor to be handled under daylight and preventing problems such as contamination of fountain solution by the unexposed photosensitive layer peeled off from the support as dirt during printing and attachment of dirt to the surface of the blanket

rubber roller that induces the deterioration of transferability of ink to the blanket roller.

[0151]

As a method for peeling and removing the unexposed photosensitive layer from the support there is preferably used a method which comprises providing the aforementioned cover sheet and then peeling it off from the photosensitive layer to remove and transfer only the unexposed photosensitive layer to the cover sheet. During this procedure, it is preferred that the unexposed photosensitive layer be peeled and removed from the hydrophilic surface of the support in such a manner that the unexposed photosensitive layer is left on the support in an amount of from 0.1 to 50% by weight based on the total solid content in the unexposed photosensitive layer rather than being fully removed.

[0152]

The removal of the cover sheet may be effected at room temperature. If necessary, the removal of the cover sheet can be effected at a temperature of 30°C to 120°C, making it easy to transfer the unexposed area.

[0153]

[Example]

The invention will be further described in the following examples and comparative examples, but the invention should not be construed as being limited thereto. The term "%" as

used herein is meant to indicate "% by weight" unless otherwise specified.

[0154]

The hydrophilic supports, ethylenic compounds and polymer binders used in the following examples and comparative examples will be described below.

[0155]

#### Hydrophilic support-1

An aluminum sheet having a thickness of 0.2 mm was degreased with a 3% aqueous solution of sodium hydroxide, electrolytically etched in a 18.0 g/l nitric acid bath at 25°C and a current density of 80 A/dm<sup>2</sup> for 15 seconds, desmutted in a 1% aqueous solution of sodium hydroxide at 50°C for 5 seconds, and then neutralized with a 10% aqueous solution of nitric acid at 25°C for 5 seconds. The aluminum sheet thus treated was rinsed, anodized in a 30% sulfuric acid bath at 30°C and a current density of 10 A/dm<sup>2</sup> for 16 seconds, rinsed, and then dried to obtain an aluminum sheet for lithographic printing plate precursor ("Support-1"). The amount of the anodized layer thus formed was 2.1 g/m<sup>2</sup>.

[0156]

#### Hydrophilic support-2

Support-1 was subjected to hydrophilicization with a 1% aqueous solution of sodium orthosilicate at 85°C for 30 seconds, rinsed, and then dried to obtain an aluminum sheet for

lithographic printing plate precursor ("Support-2").

[0157]

#### Hydrophilic support-3

An aluminum sheet for lithographic printing plate precursor ("Support-3") was obtained in the same manner as in Support-1 except that phosphoric acid was used instead of sulfuric acid. The amount of the anodized layer thus formed was 1.8 g/m<sup>2</sup>.

[0158]

#### Hydrophilic support-4

A Type HYDROPRINT aqueous developable negative-working lithographic printing plate precursor (produced by AGF) was rinsed so that the photosensitive layer was removed to obtain a polyethylene terephthalate support for lithographic printing plate precursor ("Support-4"). This polyethylene terephthalate support comprised a hydrophilic polymer layer formed on a roughened polyethylene terephthalate film having a thickness of 180  $\mu$ m to a thickness of few micrometers.

[0159]

#### Ethylenic compound-1

"PM-2" (produced by NIPPON KAYAKU CO., LTD.) (The structure of this compound is represented by the following general formula)

#### Ethylenic compound-2

"US-306H" (produced by Shin-nakamura Chemical

Corporation) (The structure of this compound is represented by the following general formula)

Ethylenic compound-3

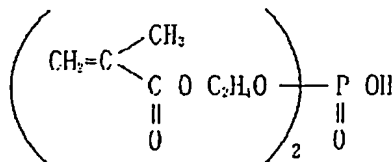
"ABPE-4" (produced by Shin-nakamura Chemical Corporation) (The structure of this compound is represented by the following general formula)

Ethylenic compound-4

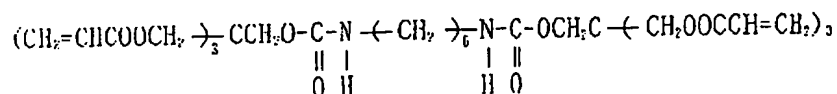
Ethylenic compound having the following structural formula

[0160]

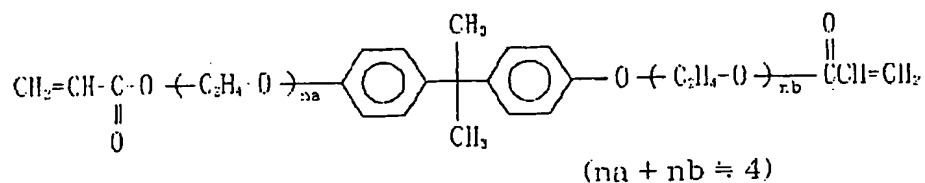
Ethylenic compound-1 (PM-2)



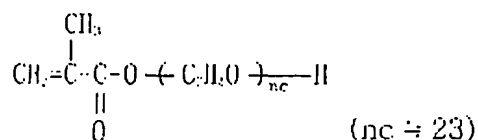
Ethylenic compound-2 (UA-306H)



Ethylenic compound-3 (ABPE-4)



Ethylenic compound-4



[00161]

Polymer binder-1

Copolymer comprising 35/20/10/35 mol-% (charged ratio) of methyl methacrylate, isobutyl methacrylate, isobutyl acrylate and methacrylic acid (Mw: 70,000)

Polymer binder-2

Into a 3 l four-necked flask equipped with an agitating blade, a reflux condenser and a nitrogen pipe were charged 80 g of 3-allyloxy-2-hydroxypropyl methacrylate, 20 g of methacrylic acid and 1.6 l of ethanol as a reaction solvent. The mixture was then heated with stirring over a 90°C oil bath. To this solution was then added a solution of 1.6 g of azobisisobutyronitrile in 400 ml of ethanol. The mixture was



then heated with stirring for 3 hours. The nitrogen pipe was then removed. To the mixture were then added 0.04 g of p-methoxyphenol and 400 ml of propylene glycol monomethyl ether acetate. The mixture was then heated with stirring for 1 hour over the oil bath the temperature of which had been raised to 100°C. Finally, ethanol was distilled off to obtain a 18% solution of ethylenic polymer binder-2 (Mw: 300,000).

[0162]

#### Polymer binder-3

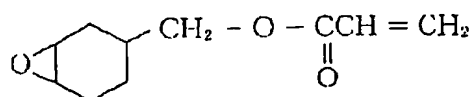
Into a 3 l four-necked flask equipped with an agitating blade, a reflux condenser and a nitrogen pipe were charged 107 g of allyl methacrylate, 13 g of methacrylic acid and 1.6 l of ethanol as a reaction solvent. The mixture was then heated with stirring over a 90°C oil bath. To this solution was then added a solution of 1.6 g of azobisisobutyronitrile in 400 ml of ethanol. The mixture was then heated with stirring for 3 hours. The nitrogen pipe was then removed. To the mixture were then added 0.04 g of p-methoxyphenol and 400 ml of propylene glycol monomethyl ether acetate. The mixture was then heated with stirring for 1 hour over the oil bath the temperature of which had been raised to 100°C. Finally, ethanol was distilled off to obtain a 20% solution of ethylenic polymer binder-3 (Mw: 180,000).

[0163]

#### Polymer binder-4

200 parts by weight of the aforementioned polymer binder-1, 75 parts by weight of the following alicyclic epoxy-containing unsaturated compound, 2.5 parts by weight of p-methoxyphenol, 8 parts by weight of tetrabutyl ammonium chloride and 800 parts by weight of propylene glycol monomethyl ether acetate were charged into a reaction vessel. The mixture was then reacted at 110°C in air with stirring for 24 hours to obtain a 25% solution of ethylenic polymer binder-4 (Mw: 75,000; acid value: 60; product obtained by the reaction of 60% of the total amount of the methacrylic acid component of the polymer binder-1 with unsaturated group).

[0164]



[0165]

#### EXAMPLES 1 - 6; COMPARATIVE EXAMPLE 1

A photopolymerizable composition coating solution having the following formulation-1 was prepared. This coating solution was spread over a support set forth in Table 1 to a dried thickness of 2 g/m<sup>2</sup> using a bar coater, and then dried. An aqueous solution of polyvinyl alcohol was spread over the coat thus formed using a bar coater to a thickness of 3 μm in an amount of 3 g/m<sup>2</sup> as calculated in terms of dried layer, and

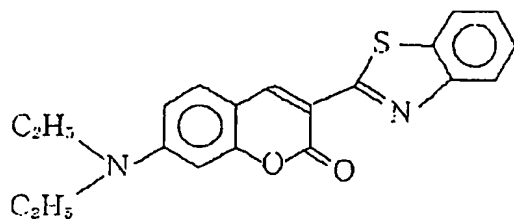
then dried to prepare a photosensitive lithographic printing plate precursor. The photosensitive lithographic printing plate precursor thus obtained was then evaluated for the following properties. The results are set forth in Table 1.

[0166]

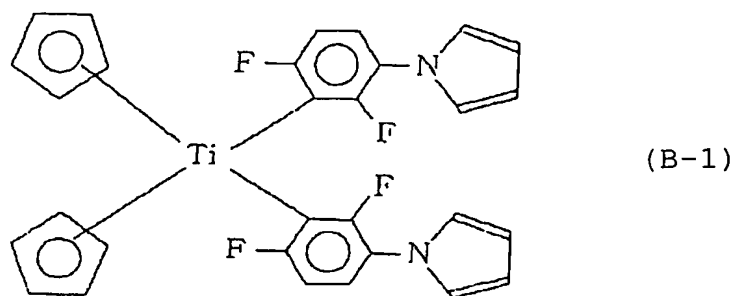
Formulation of photopolymerizable composition coating solution-1 (parts by weight)

Ethylenic monomer set forth in Table 1:	55
Polymer binder set forth in Table 1:	45
Compound having the following structural formula (A-1):	2.0
Titanocene compound having the following structural formula (B-1):	10
2-Mercaptobenzotiazole	5.0
N,N-dimethylbenzoic acid ethyl ester:	10
Copper phthalocyanine pigment:	3.0
Cyclohexanone	1,090

[0167]



(A-1)



[0168]

Properties to be evaluated

<Peel strength>

The unexposed photosensitive layer, the exposed (photo-set) photosensitive layer and the hydrophilic support were measured for gummed tape peel strength according to the aforementioned measuring method (shown in Fig. 1). The gummed tape peel strength of the support is the peel strength required to peel a gummed tape off from a support having no photosensitive layer formed thereon.

[0169]

<Sensitivity>

The photosensitive lithographic printing plate precursor was exposed using a Type RM-23 diffraction-spectroscopic light irradiating device (produced by Narumi Co., Ltd.) capable of irradiating the photosensitive lithographic printing plate precursor such that the wavelength and intensity of exposing light show a drop in the crosswise direction and a logarithmic drop in the longitudinal direction, respectively. A gummed tape ("SLIONTAPE", produced by SLIONTEC) was then stuck to the polyvinyl alcohol layer. Subsequently, the gummed tape was

peeled off from the sample. At the same time, the most unexposed photosensitive layer was peeled and removed from the support. Subsequently, the sample was mounted on the cylinder of a type Dia F-2 lithographic printing machine (produced by MITSUBISHI HEAVY INDUSTRIES, LTD.). Under these conditions, printing and development were effected on 100 sheets of paper. The optical energy required for photosetting with light of 488 nm was then determined from the longitudinal height of the printed image on the 100th printed matter. In Table 1 below, the symbol F indicates that the unexposed area was not removed and no image was formed.

[0170]

<Press life>

The photosensitive lithographic printing plate precursor was scanning-exposed at a dose of  $100 \mu\text{J}/\text{cm}^2$  using a Type PI-R air-cooled argon laser (produced by DAINIPPON SCREEN MFG. CO., LTD.), and then subjected to printing and development in the same manner as in the evaluation of sensitivity. Using the printing plate thus obtained, printing was conducted. The number of sheets of paper required until the desired image area (120 lines, 4% small points) was not formed was represented as press life. In Table 1 below, the symbol F indicates that no evaluation was conducted.

[0171]

<Image reproducibility>

The photosensitive lithographic printing plate precursor was contact-exposed to light from a high voltage mercury vapor lamp through a UGRA plate control wedge, and then subjected to printing and development in the same manner as in the evaluation of sensitivity. For the evaluation of image reproducibility, the degree of remaining of circular patch positive fine line image on the printed matter was determined (The finer the line image reproduced is, the better is image reproducibility). In Table 1 below, the symbol F indicates that no evaluation was conducted.

[0172]

Table 1

Example		Example Nos.						Comparative Example
		1	2	3	4	5	6	1
Ethylene compound (parts by weight)	1	5	5	5	5	5	5	5
	2	25	25	25	25	25	25	25
	3	25	25	25	25	25	25	25
Polymer binder (parts by weight)	1	-	-	-	45	-	-	-
	2	45	-	-	-	45	45	45
	3	-	45	-	-	-	-	-
	4	-	-	45	-	-	-	-
Support		1	1	1	1	2	4	3
Sensitivity ( $\mu\text{J}/\text{cm}^2$ )		60	50	80	90	90	70	F
Image reproducibility ( $\mu\text{m}$ )		5	4	4	5	8	4	F
Press life (10,000 sheets)		15	15	15	10	6	F	F
Gummed tape peel strength of unexposed photosensitive layer (g/cm)		50	60	70	70	80	80	*

Gummed tape peel strength of hydrophilic support (g/cm)	300	300	300	300	350	250	1,100
Gummed tape peel strength of photo-set photosensitive layer (g/cm)	*	*	*	*	*	*	*

\*: greater than 200 g/cm (Peeling occurred between the gummed tape and the photosensitive layer. The evaluation of peel strength of 200 g/cm or more was impossible.)

[0173]

#### EXAMPLES 7 - 9; COMPARATIVE EXAMPLE 2

The procedure of Examples 1 to 6 and Comparative Example 1 was followed except that as the photopolymerizable composition coating solution there was used one having the following formulation-2. The sample thus obtained was then evaluated for sensitivity, image reproducibility and peel strength. The results are set forth in Table 2.

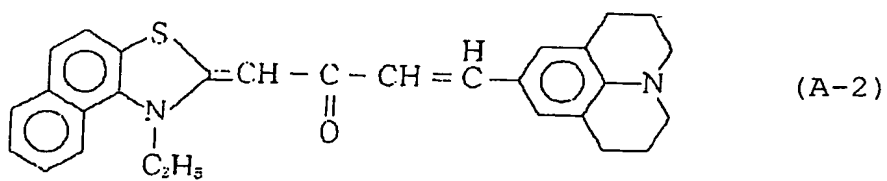
[0174]

#### Formulation of photopolymerizable composition coating solution-2 (parts by weight)

Ethylenic monomer set forth in Table 2:	55
Polymer binder set forth in Table 2:	45
Compound having the following structural formula (A-2):	2.0
2,2'-Bis(o-chlorophenyl)-4,4',5,5'-tetra (o,p-dichlorophenyl)biimidazole:	10

2-Mercaptobenzotiazole	5.0
N,N-dimethylbenzoic acid ethyl ester:	10
Copper phthalocyanine pigment:	3.0
Cyclohexanone	1,090

[0175]



[0176]



Table 2

Example		Example Nos.			Comparative Example
		7	8	9	1
Ethylenic compound (parts by weight)	1	5	5	5	5
	3	25	25	25	25
	4	25	25	25	25
Polymer binder (parts by weight)	1	-	45	-	30
	2	45	-	45	45
Support		2	2	1	3
Sensitivity ( $\mu\text{J}/\text{cm}^2$ )		70	80	70	F
Image reproducibility ( $\mu\text{m}$ )		4	5	8	F
Press life (10,00 sheets)		15	15		F
Gummed tape peel strength of unexposed photosensitive layer (g/cm)		60	70	50	F
Gummed tape peel strength of hydrophilic support (g/cm)		350	350	300	1,100
Gummed tape peel strength of photo-set photosensitive layer (g/cm)		*	*	*	*

\*: greater than 200 g/cm (Peeling occurred between the gummed tape and the photosensitive layer. The evaluation of peel strength of 200 g/cm or more was impossible.)

[0177]

#### EXAMPLE 10

The photosensitive lithographic printing plate precursor obtained in Example 1 was imagewise exposed to light, directly mounted on the cylinder of the aforementioned printing machine,

and then subjected to printing. As a result, the unexposed area was removed in the initial stage of printing to obtain a high quality printed image. The sensitivity at this point was  $60 \mu\text{J}/\text{cm}^2$ .

[0178]

#### EXAMPLE 11

A photosensitive lithographic printing plate precursor was prepared in the same manner as in Example 1 except that the cover sheet layer of polyvinyl alcohol was not provided. The photosensitive lithographic printing plate precursor thus prepared was then put in a vessel which is transparent on the side thereof opposed to the photosensitive surface of the photosensitive lithographic printing plate precursor. The photosensitive lithographic printing plate precursor was then imagewise exposed to light and evaluated under a reduced pressure in the same manner as in Example 10. As a result, a high quality printed image was obtained. The sensitivity of the sample was  $70 \mu\text{J}/\text{cm}^2$ .

[0179]

[Advantage of the Invention]

As described in detail above, in accordance with the invention, a print-developable light-sensitive lithographic printing plate precursor excellent in press life, sensitivity and image reproducibility can be provided.

[Brief Description of the Drawings]

Fig. 1 is a sectional view illustrating a method for measuring the gummed tape peel strength.

[Description of Reference Numerals and Signs]

- 1      Support
- 1A     Photosensitive layer
- 1B     Polyvinyl alcohol layer
- 2      Fixing table
- 3      Gummed tape

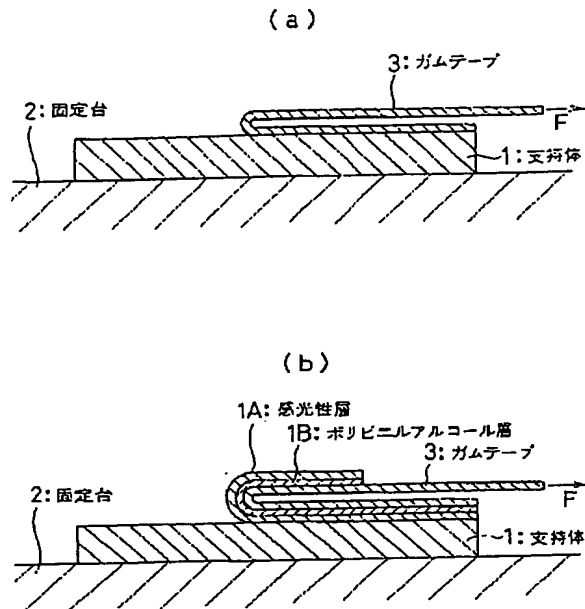


Fig. 1:

(a)

1: Support

2: Fixing table

3: Gummed tape

(b)

1A: Photosensitive layer

1B: Polyvinyl alcohol layer

2: Fixing table

3: Gummed tape